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The principal objectives of the study are to examine potentially harmful consequences of element redistribution on the environment and to assess the opportunities for economic byproduct recovery of accessory elements. Attention is focused on mining and processing methods because of the important role of technology in the redistribution and recovery of accessory elements and compounds. The study also points out research needed for improving our understanding of environmental consequences and byproduct potential of large-scale mining activities. A principal reason for the study is the expectation that major increases in domestic production of many mineral commodities will occur, either as a result of changing national policies or actions abroad, which may result in important byproduct recovery. The report does not address health problems that might result from the redistribution of accessory elements, but it does discuss redistribution pathways through which toxic elements may reach the environment, thus providing an alert to potential health hazards. Five commodities, namely, coal, oil shale, uranium, phosphates, and alumina, were selected for study.

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PART I:
Coal and Oil Shale

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Redistribution of Accessory Elements in Mining and Mineral Processing

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PART I:
Coal and Oil Shale

A Report Prepared by the
Committee on Accessory Elements

Board on Mineral and Energy Resources
Commission on Natural Resources
National Research Council

NATIONAL ACADEMY OF SCIENCES
Washington, D.C. 1979

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SUMMARY

INTRODUCTION

Scope of Study

The Committee on Accessory Elements was established to investigate the redistribution of accessory elements and compounds in future large-scale mining and processing of selected mineral materials. The principal objectives of the study are to examine potentially harmful consequences of element redistribution on the environment and to assess the opportunities for economic byproduct recovery of accessory elements. Attention is focused on mining and processing methods because of the important role of technology in the redistribution and recovery of accessory elements and compounds. The study also points out research needed for improving our understanding of environmental consequences and byproduct potential of large-scale mining activities. A principal reason for the study is the expectation that major increases in domestic production of many mineral commodities will occur, either as a result of changing national policies or actions abroad, which may result in significant impacts on the environment as well as on the potential for important byproduct recovery. The Committee does not address health problems that might result from the redistribution of accessory elements, but it does discuss redistribution pathways through which toxic elements may reach the environment, thus providing an alert to potential health hazards.

Organization and Procedure

A parent committee was organized to oversee the work of a number of panels, which were charged with investigating the redistribution problems associated with specific mineral commodities. Five commodities, namely, coal, oil shale, uranium, phosphates, and alumina, were selected for study. Individual panels, composed of four to eight members each, then investigated the problems associated with those commodities. The Coal Panel and Phosphates Panel held workshop meetings to assist in developing data for inclusion in panel reports, but the panels for oil shale, uranium, and alumina relied heavily on the literature and on private solicitations for their report input.

The Committee's overall report is divided into two parts. Part I, reflecting the special importance of fossil fuels today, combines the results of the Coal and Oil Shale Panels. Part II contains the results of investigations by the Uranium, Phosphates, and Alumina Panels.

The study is not intended to be a comprehensive assessment of all problems of redistribution or all byproduct recovery possibilities. Rather, selected commodities are studied to typify the range of possibilities and characterize the basic problems associated with increased production of mineral commodities. The selection of coal, oil shale, uranium, phosphates, and alumina for special attention is based on the expected growing importance of these commodities in the future economy of the country and the prospect of supply from domestic mining or the probable increase in the scale of domestic processing, with consequent potential for problems of redistribution of accessory elements and compounds.

In assessing the opportunities for byproduct recovery the Committee has looked primarily at the technological feasibility of recovery. It is recognized that, in addition to the market price for a product, any ultimate recovery also will depend on site-specific conditions and that to aggregate the potential byproduct production of an accessory element over total domestic production of a mineral commodity can be misleading.

Definition of "Accessory Elements and Compounds"

In this report the terms "accessory elements and compounds," "components," and "materials" refer to all constituents of a mineral deposit other than the commodity for which the deposit is primarily mined. In the usage adopted here, any one accessory element or compound may be present in amounts ranging from a trace to major proportions of a mineral deposit. Within the deposit the total of all accessory elements and compounds may be relatively small if the mineral material is of high grade. Conversely, the total may be very large if the deposit is low grade and requires the movement of huge volumes of material to recover primary materials sought. However, the problems of redistribution of accessory elements and compounds, particularly those with the greatest potential for adverse environmental impact, are only partly related to the volume of material produced. Of greater importance are the chemical nature of the materials redistributed and the transportation and dispersion mechanisms. Consequently, the chemistry of accessory elements, especially those occurring in relatively small amounts in an ore, has been given special emphasis in the various Panel reports. In addition to the naturally occurring accessory constituents associated with a mineral deposit, others may be introduced during mining and processing. These in turn may create new environmental problems from the redistribution of materials.

For this report the Committee has not adopted a single strict convention for the use of the terms "major," "minor," and "trace" to describe the quantities of accessory constituents present. However, in general it applies the term "major" to constituents present in quantities of 1.0 percent or more, "minor" to quantities in the range of

.01 to 1.0 percent, and "trace" to quantities less than .01 percent and commonly expressed in parts per million (ppm) or parts per billion (ppb).

GENERAL CONSIDERATIONS IN THE REDISTRIBUTION OF ACCESSORY ELEMENTS AND COMPOUNDS

Geologic Factors Affecting Mining and the Redistribution of Accessory Elements and Compounds

Ore deposits form through geologic processes that redistribute elements and compounds into accumulations large and rich enough to be mined profitably. However, natural redistribution processes rarely segregate only the materials sought. Other elements and compounds, of little or no present value, are also accumulated. Thus, natural redistribution processes have to a greater or lesser extent predetermined the problems to be faced in taking mineral materials from the earth and preparing them for use. Some of the problems are related to the size, shape, and distribution of the ore body in space; some are related to the chemical nature of the minerals that comprise both the principal and accessory constituents; others are related to the physical properties of the ores and surrounding host rocks that must be removed, or exposed to air and water, during mining and processing. These natural physical and chemical features of ore deposits--the geologic characteristics--may strongly affect the subsequent redistribution of accessory elements and compounds in mining and processing operations. In general, small ore bodies of highly concentrated materials pose largely chemical problems in mining, beneficiation, and processing, whereas large ore bodies requiring the movement and treatment of huge volumes of material pose both chemical and physical problems.

Deposits formed at the land surface or subsea surface--so-called bedded ore deposits--are tabular or lenticular in shape, usually extend over wide areas, and ordinarily are covered by sediments. The thickness of these deposits may be measured in feet, but the areal extent may be tens of square miles. Of the commodities discussed in this report, coal, oil shale, phosphates and some non-bauxitic aluminum ores are of this type. Such deposits, originally flat-lying, may be tilted, folded, or even broken. Their present physical configuration, depth below today's land surface, and strength or weakness of rocks overlying them will determine whether mining can be best done by surface or underground methods. The sandstone-type uranium ores that contain the great bulk of uranium mined in the United States today resemble other bedded ore deposits from a geometric point of view, although they are more lenticular and individual deposits do not extend over such large areas.

Some ore deposits found in igneous bodies extend over large areas and contain relatively low concentrations of ore minerals that can be exploited only because they are amenable to very large-scale mining operations. Anorthosites and syenites, non-bauxitic sources of aluminum, similarly occur as igneous bodies of considerable extent that might at some future time become viable sources of aluminum by virtue of very large-scale mining operations.

Most ore-forming processes are chemical and characteristically concentrate the ore minerals as sulfides, sulfates, carbonates, or other compounds that can often be solubilized more readily than the silicates that comprise the bulk of the earth's crust. Hence, exposure of ore minerals to air and water during extraction and processing can lead to increased dispersion of the associated elements to the environment.

The physical setting of the ores and surrounding rocks influences the mining methods to be used in recovery of a particular mineral commodity. Near-surface deposits, such as the phosphates of the southeastern United States, are overlain by unconsolidated or loosely consolidated materials and can be mined readily from open pits. Deeply buried deposits, such as the coals of the Appalachians, require underground-mining methods. However, in the final analysis it is the combination of chemical and physical properties of the ores and surrounding rocks and the mode and scale of mining operations that establish the potential for detrimental effects on the environment or provide opportunities for byproduct recovery of trace or minor elements.

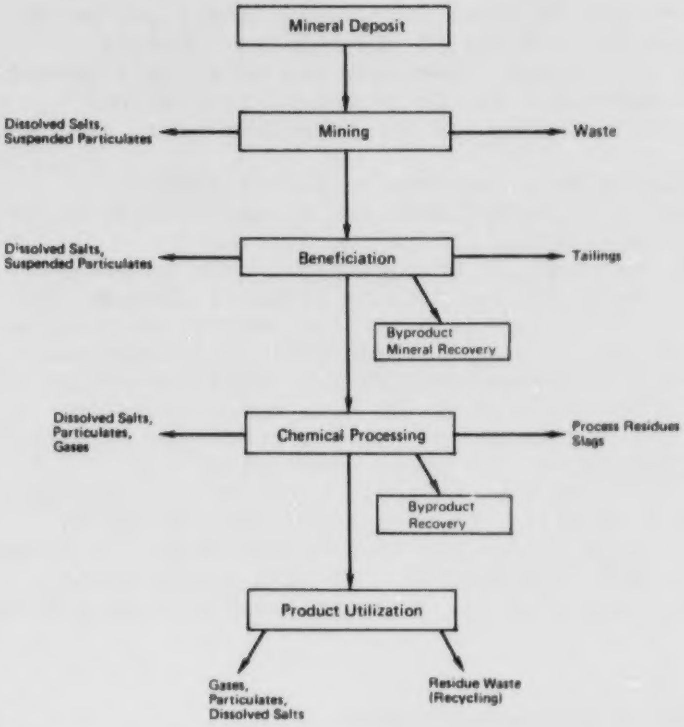
The Materials Cycle and Redistribution of Accessory Elements and Compounds

Once mining operations begin a mineral deposit is disturbed in such ways that many accessory elements and compounds are redistributed in markedly different patterns and concentrations from those that would occur by natural geologic processes. Redistribution of elements can occur during any of the steps involved in the materials cycle (Figure 1).

During mining, various elements and minerals, essentially unchanged, are made more accessible to environmental exposure. This initial increase in exposure is a result of comminution or size reduction during mining and gives rise to particulates that can be transported by air or water. Comminution also promotes the chemical reaction of minerals exposed to air and water, and commonly results in the production of oxidized water-soluble compounds that are transported as mine drainage. Waste rock or overburden is generally removed and piled away from the working area; some may be used in road and site construction but most goes into spoil piles. In surface-mining operations with high stripping ratios, significant amounts of overburden and mine waste are presently moved and even larger amounts are expected in future mining.

With most raw materials, the mined ore must be beneficiated to separate the desired minerals from the waste material. This is carried out first by comminution to a size at which the minerals are liberated from each other, followed by a concentrating mechanism for the desired ore minerals. Beneficiation technology utilizes physical or surface chemical means for separating minerals, and consequently the minerals are not changed chemically at this processing stage. Common methods of concentration involve flotation (wet process), gravity separation (usually wet), magnetic separation (wet or dry), electrostatic separation (dry), and flocculation (wet).

During beneficiation, size reduction is the most significant physical change in a raw material. However, separation of an ore into a concentrate (containing most of the desired product), and tailings (composed largely of unwanted materials), is the second stage in the


Mineral Deposit
Dissolved Salts, Suspended Particulates
Mining
Waste
Dissolved Salts, Suspended Particulates
Beneficiation
Tailings
Byproduct Mineral Recovery
Dissolved Salts, Particulates, Gases
Chemical Processing
Process Residues Slags
Byproduct Recovery
Product Utilization
Gases, Particulates, Dissolved Salts
Residue Waste (Recycling)

SOURCE: D. W. Fuerstenau, personal communication (1978).

FIGURE 1 Schematic flow diagram for materials through the materials cycle, beginning with their occurrence in the mineral deposit through their final utilization.

materials cycle where major redistributions of elements can occur. The concentrate may be utilized as the final product or, as in most cases, it is the feed material to subsequent chemical processing operations. One of the major complications of many beneficiation operations is that particles finer than 10 to 20 microns are not recovered. These fine particles can account for the loss, in some cases, of 10 to 20 percent of the valuable mineral in the ore. In addition to representing a wasted resource, their disposal may contribute greatly to air and stream contamination. Significantly, however, the beneficiation plant is the first stage in the materials cycle at which byproduct mineral recovery can occur.

Generally, chemical processing is required to convert the desired ore minerals into the chemical form suitable for use. In the case of a metal oxide, this entails reduction of the oxide to a metal, as, for example, in the production of pig iron in blast furnaces or the manufacture of ammonium phosphate in fertilizer production. Accessory element redistribution occurs through these chemical changes made in the materials. Elements in the metallic state, for instance, may accompany the metal whereas elements forming oxides may be separated and discarded as slag. In addition, volatile constituents can separate in a gaseous phase and be vented to the atmosphere.

In the processing of certain ores or concentrates, leaching with aqueous solutions may be a major separation step. Here, element redistribution follows from the discarding of leach liquid and any entrained leach residues. During chemical processing, there may be an opportunity to recover byproducts because of the chemical changes induced in the materials at this stage. Recovery can often be achieved by modification of specific processes in the flowplan, such as the installation of a dust collection system in the treatment of an effluent stream.

Product utilization accounts for a certain amount of element redistribution. Trace elements in fertilizers can be spread over large areas. Residual elements in metals and alloys can also be redistributed, depending on the eventual disposition of the materials.

Figure 1 schematically summarizes the flow of material through the stages of the materials cycle, that is, from (1) its natural occurrence in a mineral deposit, through (2) mining, (3) physical beneficiation, (4) chemical processing, and (5) product utilization (with potential recycle). Usually, all of these steps occur in developing a usable product, as exemplified by the production of fertilizer from phosphate ores. In the case of coal production for power generation, the beneficiation step is used to clean the raw coal. Chemical processing and product utilization would, however, be a combined step in boiler use. The production of coke from coal could involve all steps, as would commercial coal gasification and liquefaction. In situ gasification, however, would eliminate the beneficiation step and would combine mining with chemical processing.

PRECIS OF COMMODITY STUDIES

The following discussion summarizes the potential redistribution of accessory elements and compounds in coal, oil shale, uranium, phosphates, and alumina resulting from mining, processing, and utilization. Although there is currently no commercial exploitation of oil shale or non-bauxitic aluminum resources, these materials are discussed because of their potential use in the future production of oil and aluminum. Some of the information in the following summaries is recast later in the report under Central Findings and Observations to give special emphasis to certain topics such as potential environmental impacts and possible byproduct recovery.

Coal

In view of critical energy problems facing the nation today there is little doubt that coal will be used in increasing amounts in the years ahead. This increased use will not be without problems, particularly for the environment. There is a wide range of elements and compounds present in coals. These are redistributed in mining, beneficiation and burning, often in large quantities. The disposal of large volumes of wastes presents potentially serious environmental problems through the redistribution of proportionately large quantities of accessory elements and compounds. At the same time, however, there will be new and potential practices which, if diligently applied and studied, should significantly diminish these problems. Moreover, there will be enhanced opportunities for the byproduct recovery of various useful accessory elements and compounds.

In order to forecast the redistribution and recovery potential for different elements found in coal it is necessary to have representative data on total and average concentrations as well as the modes and variances of occurrence. Several factors influence the amount of an accessory element in a particular coal. These include: (1) composition and source of the original peat, clay, and other minerals added during and after organic matter accumulation; (2) chemical and biochemical changes through geologic time; and (3) hydrologic interchange with surrounding rocks. Despite the increasing availability of data on the distribution and concentration of trace elements in different coals the information is insufficient to permit a definitive assessment of trace-element occurrence or potential for redistribution. Yet, certain elements, such as arsenic, boron, barium, antimony, and selenium, can be identified consistently with certain coals, and patterns of occurrence are beginning to emerge. Some coals show local or regional enrichment in such elements as cadmium and zinc.

Most trace elements occur in coals in quantities less than their crustal abundances. It is in the associated shales and clays that the higher concentrations of many elements occur. This may require special attention to coal-cleaning processes to prevent or minimize the wide redistribution of deleterious constituents during burning. On the other hand, coal-cleaning wastes will become enriched in elements such as cadmium, chromium, copper, fluorine, mercury, nickel, lead, and zinc. There is little quantitative information upon which to base estimates of the composition of such wastes presently or on the disposition of these elements ultimately.

Slightly over half of the coals mined in the United States are not cleaned before use, so there is an escape of some mercury, selenium, fluorine, sulfur, boron, chromium, vanadium, and even radionuclides in present stack emissions. Large increases in the use of coal as a fuel for conventional boilers or new devices such as fluidized-bed combustion units also will increase the problems faced in disposing of elements in wastes such as ash, fly ash, slag, and products of stack-gas scrubbing. Many of the elements that escape in stack emissions or end up in waste may pose problems to the health of plants, animals, and humans. Many elements are found beneficial in some degree to certain types of plants under specific conditions. However, some are known to be detrimental to plant growth and others may be at higher levels of concentration. Prominent among troublesome stack emissions from coal-fired boilers is sulfur. Stack emissions can be transported long distances in the atmosphere and may be deposited as acid rain. The control of some stack emissions is difficult because many elements and organic compounds are concentrated on particles too small to be trapped by conventional stack-gas cleaning methods.

Coal-conversion processes, now under study in pilot and demonstration plants, raise questions of health effects that are not yet clearly understood. For example, tars produced from coal gasification and liquefaction contain relatively high concentrations of lead, arsenic, and titanium as well as organic compounds known to be carcinogens. Commercial-scale testing of control equipment is likely to be needed before we know how effectively accessory elements and compounds are removed from process streams in proposed coal-conversion operations.

The burning of increased tonnages of coal for the production of electricity will result in unprecedented quantities of solid wastes requiring environmentally acceptable methods of disposal. The solid wastes can be expected to be a major sink for many trace elements and accessory compounds, including mineral species not present in the raw coal but introduced from the country rock or developed through chemical reactions of combustion or pyrolysis. The solubility of trace elements and accessory compounds in solid wastes is believed to be as important in the redistribution into the environment as is their total concentration. We do not at present have sufficient understanding of the complex interactions responsible for the solubility, mobility, and attenuation of trace elements from coal wastes. Nor do we have much indication of whether or not various coal solid wastes and their leachates, under certain conditions, are hazardous to the biota.

Thus, leaching of contaminants from coal-waste piles is a concern, but as yet we are unable to fully interpret its nature. Recent laboratory studies show that leachates, produced under a variety of conditions, contain concentrations of boron, calcium, potassium, manganese, ammonium, lead, sulfate ions, and antimony, in amounts exceeding the water quality standards set by the U.S. Environmental Protection Agency (EPA). (In some cases, such leachates might be diluted only to a minimal extent in ground waters because of limited flow and mixing.) However, in these same laboratory experiments, a number of trace elements in leachates were immobilized by passage through earth materials. Fly ash also has been found sufficiently soluble to yield leachates under certain conditions that exceed acceptable water quality criteria for arsenic, boron, vanadium, cadmium, chromium, manganese, and selenium.

Various methods of disposing of coal wastes have been considered. Particular attention has been given to disposal in surface and underground mines. However, such disposal may increase acid mine drainage and/or increase the solubility and mobility of many accessory elements in the wastes. In addition, the effluents from coal wastes may contain appreciable amounts of processed organic matter, such as coal-liquefaction residues, and there may be some toxic products associated with them. On the other hand, increased accessibility of some trace elements may be beneficial to plants, animals, and humans under certain conditions, and care should be taken to identify the beneficial as well as the deleterious aspects of accessory elements redistribution.

There is considerable potential for byproduct recovery of accessory elements from coal products, and future mining and processing should consider this potential. Trace-element recovery from coal-preparation-plant refuse may be economically attractive because the cost of mining and most of the preparation costs may be charged to the coal and not against the byproduct. However, it is difficult to assess the prospects of economic recovery of accessory elements because the amounts and distributions of those elements at a site are incompletely known, and the market conditions determining value will vary widely. Except for sulfur, there is only limited information on the concentrations and distributions of accessory elements and compounds in coal wastes. With better data it will be possible to estimate the extent to which future problems created by increased amounts of wastes associated with coal mining, beneficiation, and burning can be offset through the recovery of mineral materials from coal-waste products.

Oil Shale

Oil shale resources in the United States are very large and probably contain more than 2 trillion barrels of oil, although much of this is probably not recoverable. No commercial-scale production of oil from oil shale is yet under way, but the future development of this resource could supply a significant part of the U.S. oil requirements over the long term. This in turn will require the mining and processing of vast quantities of raw oil shale and the disposal of resulting waste products. Because there has been no industrial development of oil shale, our knowledge of accessory elements and their redistribution is limited. Yet, some basic data on accessory element content is available and this, together with knowledge obtained from pilot and large-scale retort tests, permits an identification and assessment of many of the problems that will be faced in future exploitation of our oil shales.

The principal oil shale reserves of the United States are found in the Green River Formation of Utah, Wyoming, and Colorado. They contain relatively high concentrations of an insoluble organic material, kerogen, from which the oil is derived. Locally, halite, nahcolite, and dawsonite are present in the shale in potentially commercial quantities. Nahcolite is a potential source of soda ash and dawsonite a source of aluminum. A wide spectrum of trace elements is associated with oil shale deposits and the potential for element redistribution is high. Because of low rainfall and the high concentration of salts associated with mineral strata in the Utah-Wyoming-Colorado region, surface and ground waters contain large quantities of dissolved salts leached from the shales and associated strata. For many of these waters the content of sulfur, chlorine, fluorine, boron, iron, arsenic, and manganese exceeds public health standards before any industrial development is undertaken.

Oil shale may be mined by open-pit or underground methods and subsequently retorted above ground, or it may be retorted by *in situ* methods. Each method disturbs large quantities of material and increases the probability for redistribution of accessory elements. Open-pit and underground mining may require the disposal of highly saline subsurface water as well as the disposal of huge volumes of waste rock. The main problems in the disposal of overburden from open-pit mining or waste rock from underground mining involve leaching of soluble minerals, which could contaminate surface and ground waters. Erosion of waste piles could also be a problem.

The extraction of oil from oil shale will be accomplished through underground *in situ* retorting or by surface retorting. *In situ* processes would retort 75 percent or more of the rubblized shale in underground retort chambers. If the chambers are sealed from ground-water zones, the redistribution of elements would be limited to pyrolysis products removed from the retort as gases and liquids.

The composition of gaseous products would depend on the composition of the oil shale, the retort temperature, and the composition of air used to support combustion. Low-Btu gas produced in the retort primarily contains nitrogen, carbon, oxygen, hydrogen and sulfur. There is little information on the trace-element content of the gas phase, but it is likely that mercury, arsenic, selenium, and possibly fluorine will be present. Water vapor condensed from the gas phase contains primarily ammonia and carbonates, with traces of some organic substances and sulfur-bearing compounds. If these gases were used to generate electrical power, the resulting nitrous oxides, sulfur dioxide, carbon dioxide, and water in the off-gas would probably be emitted to the atmosphere.

Liquid products are principally shale oil and retort water which is volatilized with the oil and must be physically separated. Accessory elements in shale oil from simulated in situ retort tests include arsenic, cadmium, fluorine, selenium, sulfur, nitrogen, iron, nickel, cobalt, mercury, phosphorus, and titanium. However, little data are available on how these elements might be redistributed. In situ process demonstrations have resulted in retort waters containing ammonia, carbonate and bicarbonate, sulfur, chloride, and dissolved or suspended organic compounds. Smaller quantities of calcium, magnesium, and sulfides are present, as are suspended shale fines. Trace elements in retort water include arsenic, boron, fluorine, mercury, and selenium.

If underground retort chambers are not sealed, a new set of potential problems will exist because liquids and retorted shale leachates may have access to ground waters. The use of a mixture of ammonium nitrate and fuel oil as an explosive for rubblization prior to retorting could also result in enrichment in nitrogen, which, as nitrate, is highly soluble and hence a possible ground-water contaminant.

Surface retorting will also result in the redistribution of elements into gaseous and liquid phases of the process stream, and in addition will generate large volumes of retorted shale that will require disposal in an environmentally acceptable manner. Presently available qualitative data suggest that most of the trace elements, including beryllium, cadmium, chromium, cobalt, fluorine, lead, manganese, molybdenum, nickel, vanadium, and zinc, are retained for the most part in the retorted shales. However, arsenic, nickel, vanadium, and zinc are also redistributed to the oil in significant quantities. Arsenic, mercury, selenium, and zinc have been detected in the off-gases. Particulate emissions during crushing and moving the raw shale may also result in some redistribution of elements. Fluorine is especially likely to be an important element in particulate emissions.

The main potential for byproduct recovery in the mining and processing of oil shales lies in the recovery of aluminum from dawsonite and soda ash from nahcolite. It is possible that the treatment of dawsonite by leaching processes would result in the redistribution of elements associated with the dawsonite. But nahcolite is unchanged chemically by crushing, sorting, and screening to recover the fine nahcolite particles. Some commercially valuable sulfur, ammonia, and petroleum coke might be obtained from the shale oil when it is treated to reduce its nitrogen and sulfur content prior to pipeline transportation.

Redistribution of accessory elements during oil shale processing will occur primarily in the disposal of waste products. Three major solid and liquid waste products--off-gas scrubbing wastes, retorted shale, and retort process water--will require disposal. There may also be some prerefining wastes generated.

Off-gas scrubbers will contain carbon, nitrogen, and sulfur along with some trace elements. The composition of the wastes will depend on shale composition and retorting variables such as the extent of gas recycling, which will vary in turn with location and retorting technology. The disposal problems with retorted shale are notable because of the huge volumes of waste, as much as a million or more tons per day, that might be produced by a mature industry. Redistribution of trace elements could occur through loss of particulates by wind and water erosion, and by leaching of retorted shales. Due to the physical properties of retorted shale, erosion losses will be substantial if waste piles are not stabilized. Disposal of retorted shale or in situ retorting close to the water table or within the saturated zone would present opportunities for the redistribution of elements and consequent ground-water pollution. Except for arsenic, fluorine, mercury, and perhaps antimony, most trace elements are retained in the retorted shale, but only limited information is available on their leachability with time or their possible environmental impact. Preliminary studies indicate elements most likely to be leached are fluorine, molybdenum, arsenic, and lithium.

Potential problems related to organic residues in retorted shales, such as complexing of trace elements and solubilization of organic residues, as in the case of inorganic residues, will depend on processing methods, management of wastes, and environmental variables. Several investigations are now under way to establish the effects of these variables on the mobility of inorganic and organic residues.

A foremost environmental concern in the leaching of retorted shale is the potential impact on the salinity of the Colorado River. Lower Basin salinity might be increased by reducing the flow of water into downstream regions. Uncontrolled mine dewatering, runoff from retorted shale disposal piles, or percolation of saline leachate into local hydrologic systems would also increase Lower Basin salinity. These effects might well be greater in drought years. On the other hand, the withdrawal and subsequent treatment of large volumes of highly saline water from saline aquifers or surface streams might decrease the salinity of the river.

Prerefining wastes could also result in the redistribution of accessory elements, but prerefining practices are not well established and data on the compositions of these wastes and on the potential movement of accessory elements are very limited.

Uranium

The mining and processing of uranium ores pose special problems with respect to environmental hazards because of the radioactive nature of certain accessory constituents. Unlike many other mineral commodities the future mining of uranium is not apt to involve a large total volume of ore. It is anticipated that as much as 85,000 short tons of ore per day may be milled by 1985 and perhaps twice this amount by the year 2000, depending on the acceptance of the nuclear power option in the years ahead. Part of the increased tonnages mined will result from an increased demand for uranium fuel, but part will result from the lower grade of ore that is expected to be mined. Nevertheless, the total tonnages will remain modest and compared to other commodities the redistribution of accessory elements as a result of mining and processing can be expected to be of limited volume. The uncertainty of the future demand for uranium fuel makes it difficult to make a rigorous assessment of the problems of element redistribution. However, it is possible to identify and evaluate the kinds of problems that will be involved in future mining of uranium ores.

It can be expected that domestic uranium production will continue to come from coarse clastic rocks, about half of which will be mined by surface methods and half by underground methods. Elements associated with uranium ores from sandstone-type deposits include selenium, vanadium, molybdenum, iron, cobalt, copper, beryllium, arsenic, nickel, lead, silver, and zinc, plus the daughter products of natural radioactive decay of uranium. The range of element concentrations is rather broad and reflects the erratic occurrence of specific elements in sandstone-type deposits. The amounts of these elements in uranium ores is known with some degree of certainty only for the Colorado Plateau ores. Only very limited information is available on ores from other mining districts.

Some elements associated with uranium ores are essential to our industrial economy, but all have sources of supply much greater than that involved in U_3O_8 production. Some vanadium, molybdenum and copper have been recovered as a byproduct of processing some sedimentary-type ores, but in general there is little incentive to recover accessory elements except when this is necessary as an environmental or product purity consideration. Some molybdenum has been recovered and marketed as calcium molybdate or ammonium phosphomolybdate. Copper has been recovered in some past uranium-milling operations, but presently only one plant has copper recovery facilities. Vanadium has likewise been recovered from some past milling operations. At current prices there is an incentive to recover this element only if it occurs in mill feed in amounts of .2 percent or more. In the Uravan mineral belt vanadium is present in quantities that make recovery worth considering.

Attempts have been made to extract some elements such as rhenium, scandium, and selenium in uranium ore processing, but the prospects for economic recovery are remote or nonexistent in today's markets. Thorium-232 has been recovered as a byproduct or coproduct of uranium processing in other countries, but no U.S. ores contain enough of this element to be worth recovering. It has, however, been present in sufficient quantities to require care to prevent contamination of the uranium product.

The major concern in the redistribution of accessory elements associated with uranium ores involves the loss of radioactive products to the environment. About 85 percent of the natural radioactivity is contained in the tailings that result from processing. Mining and milling make the radionuclides more available to water, plants, and animals via losses from finely ground tailings in waste dumps. Exposure may result from windblown dust containing thorium-232 and radium-226, inhalation of radon-222 (radon gas), gamma radiation, or contamination of ground waters.

Disposal of wastes is thus a significant problem to be resolved in the future mining of uranium ores. The nature of this problem will not change with the mining of increased tonnages of ore but the magnitude will. Care must be taken to stabilize or isolate radioactive waste products. It has been found that a clay cap over tailings can substantially reduce the exposure from radon-222.

Some earlier mining and milling operations resulted in excessive ground radiation near old tailings piles. There has been, in addition, some contamination of stream waters with radium-226, selenium, and vanadium--to the extent that water quality did not meet state water quality standards for irrigation or livestock. A covering of the waste piles can lessen greatly such contamination of the environment. It seems likely, however, that most of the past problems involving the redistribution of accessory elements in mining and processing uranium ores can be minimized in the future through strict adherence to current environmental regulations.

Two processing methods, variations of acid leaching and alkaline leaching, are used to recover uranium. The occurrence of byproduct-type elements in the ores is completely incidental to the operation and is of importance only insofar as they affect the processing costs. Rarely are accessory elements worth recovering for their income potential, but it may be necessary to give them special treatment to avoid product or environmental contamination.

It is likely that most future mining and processing of uranium ores will be carried out with technology now employed. An exception to this is the possible further development and application of *in situ* recovery methods in which uranium is leached underground from the host rocks. *In situ* leaching might mobilize accessory elements such as arsenic and selenium in the ore and ground waters might then become contaminated. Our knowledge of the effects of *in situ* processing, however, is very limited.

Phosphates

Phosphates provide a major underpinning of our agricultural industries and are thus one of our most vital resources. The United States has large reserves of phosphates and is not dependent on foreign imports. Most of these resources are located in the coastal plain of Florida, Georgia, and North Carolina, and in the western mountain states of Idaho, Montana, Wyoming, and Utah. Lesser resources are present in Tennessee. Most of the domestic deposits are mined by open-pit methods and most of the phosphate product goes into wet-phosphoric acid manufacture and ultimately into fertilizers.

Phosphate mining and processing operations result in major redistributions of accessory elements and compounds. A perspective of the magnitude of potential redistribution problems, both in terms of environmental impact and byproduct recovery of associated elements, may be gained from the fact that the United States produced about 47 million tons of phosphate rock in 1977. This quantity of phosphate rock contained 5 to 10 thousand tons of accessory uranium, an amount that is significant even though the average uranium content of phosphate rock is only .01 percent or slightly more. Redistribution problems begin with mining operations when uranium-bearing waste rock is excavated and moved to other locations where radon gas may escape into the atmosphere unless the waste material is buried or capped with a layer of nonradioactive overburden. In beneficiation of phosphate rock, where the matrix is crushed and treated to recover phosphate concentrates, large quantities of wastes, both as coarse tailings and as very fine materials called slimes, are produced. More importantly, accessory elements and compounds are redistributed to these wastes. Although most uranium is contained in the pebble and concentrate products, significant amounts are lost in slimes and lesser amounts in sand tailings. This redistribution of uranium and its decay products, like that in spoil piles, is of note because of radon emissions that could adversely impact on land use and habitation.

It is in the chemical processing of phosphate concentrates that most opportunities for redistribution of accessory elements and compounds occur. In acidulation processes, especially, many elements and compounds become highly mobile and find their way into stack gases, process waters, and process solid wastes, and to lesser extent into recovered byproducts and manufactured products. Of particular importance is fluorine which makes up 3 to 4 percent of the phosphate concentrates and which can impact adversely on the environment if allowed to escape. Large quantities of fluorine are evolved in wet-phosphoric acid production and find their way into stack gases. However, these gases are scrubbed to remove most of the fluorine, although small amounts of this element do escape into the atmosphere. Fluorine may also migrate via process waste water to gypsum settling ponds where most of it is precipitated and contained as solid-waste products. There may be some fluorine emission into the atmosphere from storage-pond waters, and escape through ground-water seepage is also a possibility. However, fluorine emissions are now carefully controlled by state and federal regulations to minimize their impact on the environment.

Uranium, which is likewise a potential contaminant of the environment, is also mobilized in chemical processing of phosphate rock and finds its way principally into liquid and solid wastes. Both fluorine and uranium are recoverable as byproducts in chemical processing of phosphate ores. Uranium recovery, in particular, is becoming economically attractive, and some phosphoric acid producers have begun to recover byproduct uranium. Other producers are constructing facilities for this purpose. The phosphate industry could become a significant source of uranium supply in the future. Other accessory elements, such as the rare earths, vanadium, and others, are recoverable. At current prices, there is little economic incentive to separate these constituents.

Redistribution of accessory elements and compounds can occur at all stages of exploiting phosphate resources, including mining of ores, beneficiation, rock drying, rock transportation, waste disposal, chemical processing, and even the application of fertilizer products to the soils. The basic technology to control potential environmental hazards is known. Regulations are in effect to minimize environmental problems.

Alumina

The United States presently depends almost entirely on foreign sources for its aluminum supply. However, increasing costs of bauxite from traditional overseas sources and growing instabilities in the international market should encourage the United States to consider the potential of various domestic sources. The United States has extremely limited resources of bauxite, the conventionally used source of aluminum. However, it has large quantities of non-bauxitic aluminum resources. The most attractive of these as potential sources of aluminum are high-alumina clays and alunite deposits. Lesser interest attaches to dawsonite in oil shales, anorthosites, and nepheline syenites. The redistribution of accessory constituents in any processing for recovery of alumina would depend on the type of material used as mill feed and the specific recovery process used.

High-alumina clays are composed largely of kaolin and contain over 30 percent alumina. The principal deposits, totalling more than 9 billion tons, are in Georgia and South Carolina. They are amenable to open-pit mining and can be processed by several different methods. Some impurities are present, but very few that might cause environmental problems. Most of the liquid, solid and gaseous wastes can be controlled by known techniques. There could be some potential for byproduct recovery though the economics of byproduct production are not attractive at present. The current mining of clays and disposal of waste products are carried out under state-controlled environmental standards and procedures and no serious environmental problems are envisioned.

Alunite occurs in vein and bedded sedimentary deposits and as disseminated aggregates in igneous rocks. Vein and bedded deposits rarely exceed 1 million tons in size and are not likely to be sources of alumina in the foreseeable future. But disseminated deposits are very large, up to 100 million tons. Those containing 25 to 30 percent alunite are the most promising as potential sources of alumina. But alunite mineralization is erratic in many deposits and only a few ore bodies occur with sufficient consistency of mineralization to be exploitable. Any mining of alunite deposits would most likely be done using surface-mining methods, and involve drilling and blasting of the generally hard rock. Large volumes of material would be moved and disposal of wastes might be a problem depending on the site and disposal plan. Wastes from mining consist primarily of overburden and waste rock associated with the alunite ore. Oxidation and leaching of pyrite in spoil piles could occur and sulfuric acid and soluble ferric sulfates produced. These could become environmental contaminants.

Either caustic-leach or acid-leach processes may be used to treat the alunite. Both processes produce potassium sulfate as a coproduct. Sulfuric acid also can be recovered as a byproduct from caustic-leach processes. There may be some potential for byproduct recovery of vanadium, gallium, and other metals associated with alunite deposits, but to date there has been little interest in this.

The Alumet caustic-leach process for treating alunite results in wastes that are composed largely of silica. These can be slurried to tailing ponds for disposal. The Alumet plant plans to process phosphate rock with sulfuric acid generated in producing alumina, and this could result in the production of contaminants discussed earlier. Ore roasting will produce varying amounts of sulfur dioxide and particulate emissions.

Acid-alumina-leach processes may solubilize some elements not taken into solution by caustic leach, but insufficient data are in hand to characterize the accessory constituents or assess possible environmental impacts.

Dawsonite, an aluminum-bearing carbonate, makes up about 10 percent of the oil shales over a large part of the Piceance Creek Basin in Colorado. In places the rocks contain as much as 3 weight percent extractable alumina and are a potential source of aluminum. The most likely method of recovering alumina would be the leaching of retorted oil shale with a mild caustic solution. The recovery of alumina might well be undertaken in conjunction with oil recovery and hence have the same set of problems relating to the redistribution of accessory elements. Oil shale retort waters are known to have high concentrations of uranium, arsenic, tin, fluorine, iron, and boron, and similar concentrations might be expected in process waters used in recovery of alumina. However, there is little detailed information on the mobilization and fate of accessory elements in the several processes proposed for alumina recovery. Byproduct potential would probably be similar to that of processing oil shales for oil, with soda ash a principal byproduct consideration. Disposal of waste rock would be a major environmental concern.

Anorthosite is an igneous rock characterized by a relatively high alumina content, ranging from 25 to 30 percent. It is not likely to be mined in the foreseeable future. Anorthosites occur in several localities in the United States, with the best known occurring in the Adirondacks. The major anorthosite bodies are igneous intrusions that occupy areas as large as 1,000 square miles. Resources are estimated to be in the billions of tons. Few accessory elements are present in anorthosites in significant amounts and none are presently known to have any economic or environmental importance.

If anorthosite bodies were to be mined, open-pit methods would be used. Large volumes of material would be moved and there might be problems of blowing dust. There might also be a problem with leaching of waste piles, particularly the sintered and leached products from which the alumina had been extracted, although little information is currently available on the behavior of accessory elements during sintering and subsequent leaching.

Nepheline syenites are coarsely crystalline igneous rocks occurring in small intrusive masses rarely exceeding a few square miles in extent. They contain alumina ranging in concentrations from 17 to 23 percent. A number of associated accessory elements are present in amounts 5 to 10 times greater than their crustal abundances, but only cerium, lanthanum and niobium might have some economic significance.

Like anorthosites, the nepheline syenites, if mined, would involve open-pit methods to remove large volumes of rock that would be treated by sintering/leaching processes. Intensive leaching could lead to increased alkalinity of surface runoff. However, there is very little detailed information on the mineralogy, accessory element content, and tonnages of nepheline syenite deposits or on their suitability for alumina production. The small size of nepheline syenite deposits and their relatively low content of alumina make it unlikely that they will be developed for alumina in the United States in the foreseeable future.

CENTRAL FINDINGS AND OBSERVATIONS

Availability of Data

Coal

Data on the distributions and concentrations of some accessory elements in coals from different areas are extensive. However, because coal reserves are present in billions of tons and because wide variances exist in the distributions of accessory elements, information on which to base an assessment of accessory element redistribution or byproduct potential must be considered inadequate. The data base is insufficient to predict accurately the mean concentrations or the range of elements in the coals of different coal basins or even of individual beds. However, we do have a fairly broad view of the kinds and amounts of accessory elements in U.S. coals, and for some areas, such as the Illinois Basin, the data are rather comprehensive. For many areas, suites of accessory elements can be consistently identified in certain coals, and for some major coal seams, patterns of occurrence are beginning to emerge. Because values reported for accessory elements in various coals come from limited samples and may differ by 1 or 2 orders of magnitude, it is unlikely that reported concentrations of a particular element in a whole coal will be representative of that coal. An accurate representative chemistry is important in characterizing a coal for a particular use and for considering the potential for byproduct recovery of certain elements.

Knowledge of the physical and chemical characteristics of accessory elements in coal-cleaning wastes is likewise limited and inadequate to assess refuse disposal problems, such as ground-water pollution, or to assess the potential for byproduct recovery. Nor, except for sulfur, is it possible to quantify the relationship between raw-coal and clean-coal analyses. For coal-conversion-plant emissions there are inadequate data on the distribution of many trace elements, and organic emissions from coal conversion are largely uncharacterized. Furthermore, the amount of data is limited on the concentrations and solubilities of accessory elements in ash and sludge that might be disposed of in underground mines, strip-mined areas, or landfills that are subsequently buried.

Much information is available on different aspects of coal mining, beneficiation, burning, and treatment of wastes, but the total amount of data is sparse relative to the magnitude of the resource and requirements for future use. Until a broader data base is available, it will not be possible to predict with reasonable assurance the commercial future of recovering accessory elements or the total environmental impact of coal utilization.

If the problems of future large-scale mining of coal are to be adequately addressed our fundamental geologic and chemical knowledge of coal will need to be greatly expanded. In addition, the complex interactions of accessory elements and compounds during beneficiation, burning, and waste disposal will need intensive study. Of special importance are studies of the composition and disposition of wastes, effluents, and emissions associated with coal-conversion processes. These processes, inadequately understood at present, are likely to become highly significant in future exploitation of coal resources. Baseline studies should be made now so that future coal-conversion problems will not suddenly appear without a sound basis for resolution.

Oil Shale

There is presently no commercial production of oil from oil shale and no history of commercial production from which data on the redistribution of accessory elements from oil shales can be obtained. Information on the composition and behavior of accessory constituents in oil shales comes from fundamental scientific and engineering studies made over the years, and recent pilot- and demonstration-plant operations. There are more chemical and mineralogical data on the raw shale and surface waters than on products of processing or on ground waters associated with oil shale regions. Information is now being developed on the composition of process water, retorted shale, leachates, and stack gases as well as the possible impact on the terrestrial environment, and surface and ground waters. However, there is as yet an insufficient understanding of mechanisms and pathways of redistribution of accessory elements for environmentally sound planning and management of large-scale mining and processing operations. To develop this understanding will require continued and expanded efforts to characterize the chemical and physical nature of process-stream materials that may reach the environment as a result of oil shale extraction processes. These efforts in turn should be coupled with studies of atmospheric and hydrologic transport of accessory constituents. Basic atmospheric and hydrologic data and transport models are needed to assess the impact of gaseous effluents on flora and fauna, water use and movement, and the mobility and effects of salts, trace metals, and trace organics in surface and ground waters. For predictive purposes it is essential that the basic inventory and interactions among accessory elements and compounds at all stages of mining, beneficiation, chemical processing, and waste disposal be broadened to include principal technologies and time-dependent changes. This will require not only intensive laboratory investigations but also full-scale process demonstrations as well as monitoring of waste effluent movements.

Uranium

Except for the Colorado Plateau ores there is relatively little information on the concentrations and distributions of accessory elements in uranium ores. Even for the Colorado Plateau deposits, for which abundant information exists in the literature, the data are incomplete and pertain mostly to hand specimens of a few hundred grams. These data are not reflected in the concentrations of ore shipped to mills. The reason is that accessory elements are erratically distributed within deposits and concentrated either in organic-rich pockets, in discrete sedimentary beds, or secondary structures ("rolls"). Ore is homogenized in mining and milling, and the range of concentrations in mill feed and concentrate reduced from its original broad span. Available accessory element data therefore reflect average concentrations within large volumes of ore.

The only consistent data are from Colorado Plateau ores mined in the 1950s, but they suffer because older analytical methods were not as accurate as those used today. Also, in earlier mined ores no analyses were made for certain elements that are routinely determined today. Furthermore, no analyses of accessory element concentrations were made of uranium ores from Wyoming, Texas or New Mexico. However, the U.S. Geological Survey and a number of State Surveys are now beginning to collect and evaluate accessory element data from current production and potentially commercial sites.

Phosphates

Geological and geochemical data on phosphates have accumulated over many years, primarily with the development of the fertilizer industry, and our information base today is extensive. Except for probable offshore deposits, our domestic phosphate resources are well known. The chemical compositions, mineralogical forms, and structural properties of phosphates have been extensively studied and are well documented. More importantly, the behavior of various elements and compounds in chemical processing for fertilizer production is, with some exceptions, well known, thus providing a firm base for dealing with many potential environmental impacts. However, specific problems, such as ground-water contamination, need further study to document the geochemical pathways of accesory elements and compounds into the environment. We do not yet have sufficient detail on radon emissions from spoil piles. Nor do we have complete understanding of the impact of fluorine emissions from processing-plant cooling-pond waters. Additional data are needed on the long-term cumulative effects of fertilizer application to farm soils and on the plant uptake of trace elements. Finally, if phosphate ores are used extensively in the future for their uranium content, it will be necessary to develop additional data on removal of certain constituents from ores and to investigate chemical pathways through which contaminants might escape into the environment.

It will also be important to further develop or improve methods for economic mining and processing of phosphate deposits that are deeper and lower grade than those being mined today. Future studies should not only seek efficient means for physically removing the deeper deposits from the ground but also improved ways of beneficiating low-grade ores. It will be especially important to seek ways to minimize the use of water. With decreasing grade of ore it would also seem desirable to investigate further the economic recovery of byproduct constituents. Waste disposal and land reclamation will continue to be major problems requiring continued research. Improved methodology for waste disposal should also involve ways of recovering phosphates lost to slimes.

Alumina

There is presently no commercial production of alumina in the United States from high-alumina clays, alunite, dawsonite, anorthosite or nepheline syenite. Basic data on concentrations of specific accessory elements in these deposits are limited and are known primarily from general studies or from investigations involving other commodity extraction potential. Thus, a good deal of information is available on southeastern U.S. clays which are presently processed for their use in paper manufacture and related commercial applications. However, more pilot-plant information on processing of clays for their alumina content is needed before a rigorous assessment of potential environmental problems can be made.

Alunite deposits have been studied fairly extensively, especially those in Utah, and the kinds of accessory constituents are reasonably well known and their potential distributions in nature have been estimated. In addition, all of the mining and waste disposal techniques necessary for alunite mining are well developed in other sectors of the mining industry and most of the technology to be used in processing has already been well established in other metallurgical applications.

What is known of dawsonite associations comes from early basic studies of the oil shales and more recent investigations specifically related to recovery of oil from those rocks. However, the mineral and organic hosts of most trace elements, their stratigraphic distributions, and associations of accessory constituents in dawsonitic oil shale are still poorly known. Furthermore, almost nothing is known about the mobilization and fate of accessory elements in the several processes proposed for alumina recovery. Studies should be made of the mass balance, transport, and fate of accessory elements not only in processing but also in disposal of retorted shale wastes.

Basic mineralogical data are available for the anorthosites and nepheline syenites, but very little information exists on the accessory element content of these rocks. Complete chemical analyses of representative samples of anorthosites and nepheline syenites are not available in sufficient quantity to permit an adequate review of the potential for redistribution and byproduct recovery of accessory elements. Data are particularly lacking on the behavior of accessory elements during sintering and subsequent leaching operations that would be used in recovering alumina from these rocks.

If non-bauxitic resources are to be used as a source of alumina the behavior of accessory elements during processing and disposal of wastes will need to be understood. With few exceptions one can only speculate today about the redistribution and behavior of accessory elements in the mining and processing of non-bauxitic materials.

Environmental Impact of Redistribution

Coal

A wide variety of accessory elements is found in coal and the potential for redistribution of accessory elements and compounds into the environment at all stages of mining, beneficiation, burning, and disposal of wastes is large. Coal mining has been an important cause of redistribution of accessory elements in the Appalachian and Eastern Interior Coal Regions. If strip-mined areas are left untreated, the redistributed overburden can become extremely acid due to the weathering of pyrite and subsequent leaching of the spoil piles. Where spoils are used to backfill a mine, highly mineralized leachates may develop and percolate into the ground-water system. The drainage from both strip and underground mines can be highly acidic, and where mines have been abandoned this drainage is the greatest single source of acid mine water and probably the most difficult environmental impact to control. Acid mine drainage is not a significant problem with most western coals because they contain very little pyrite.

Effective coal-cleaning processes have been developed for removing many of the contaminants from coals, but there still remains a significant potential for environmental pollution. Many contaminants still find their way into combustion wastes. Both the solid and gaseous wastes from power plants pose a particular concern. It is obvious, though, that cleaning up one source of waste, such as stack gases, transfers the contamination problem elsewhere, as in the wet sludges resulting from flue-gas desulfurization. Thus, the environmental tradeoffs of different disposal streams need careful analysis. Despite the recovery system employed, some level of contaminants, such as arsenic, selenium, sulfur, fluorine, and mercury, pass through the stacks of present coal-fired power plants. Some two dozen elements are of concern.

Elements escaping into the atmosphere affect the surrounding vegetation, with the most severe impacts confined to relatively short distances from the power plant. The severity of injury resulting from gaseous emissions can be very great from either acute or chronic air pollution conditions. Of the trace elements that are emitted, many are associated with fly-ash particles too small to be effectively trapped using conventional scrubber and precipitation equipment. Some are emitted mainly in the gaseous state, particularly the oxides of sulfur, nitrogen, and carbon. Selenium, mercury, antimony, arsenic, cadmium, and molybdenum, as well as fluorine, may also escape in this manner. However, new techniques (fabric filtration, baghouse temperature control) in combination with conventional stack-gas scrubbing may provide a measure of increased control for particulate and gaseous emissions.

High-Btu gasification processes carried out under elevated temperatures and pressures produce two major effluents--solid ash and slag, and liquid wastes from scrubbing raw gas. Each of these effluents is a potential conduit for accessory element redistribution.

Increased development of coal-conversion plants could result in the production of large quantities of waste, largely in solid form but with lesser streams of liquid and airborne wastes. Any future large-scale use of conversion plants will require the disposal of vast amounts of wastes that may contain solid chemical compounds not in the original coal. More data are needed to assess the potential for redistribution of elements in different effluent streams and final waste disposal sites under differing conditions.

The proposed underground gasification of coal is likely to pose the same environmental problems as conventional coal extraction techniques.

There may be temporary disruption of the land surface as well as subsidence similar to that resulting from underground coal mining. *In situ* gasification will also result in the mobilization of accessory elements that could contaminate ground-water supplies. However, there is no good baseline data on element mobilization in subsurface coal-conversion processes. Such data will come only as sites become operational or demonstration projects provide commercial-scale results.

The pH of the enclosing medium is one of the most important factors affecting the solubility of accessory elements in coal solid wastes. Many of these wastes contain sulfide minerals that can oxidize and acidify the water. Acid water in turn may become charged with heavy metals from the solid wastes. Knowledge of coal-ash solubility and methods for environmentally acceptable disposal of coal ash is still incomplete. Laboratory studies indicate that rapid leaching occurs for some accessory elements, but it is not known whether this is restricted just to the surface of the ash deposit or characterizes the full thickness of ash. The disposal of wastes produced from coal-combustion and coal-conversion processes may affect the quality of local surface- and ground-water systems, especially if the disposal areas are subject to seepage or are in proximity to aquifers.

The opportunities for environmental contamination from coal mining, processing, burning, and waste disposal are many. This is implicit in the large number of accessory elements, many of them toxic, found in raw coals and processing wastes. Considered in terms of the tremendously large quantities of coal being mined today and the expectation that more than a billion tons of coal per year may be mined in the not-too-distant future, the potential impact of redistribution of accessory elements into the environment becomes severe. A better and more thorough understanding of redistribution mechanisms and pathways is needed to prevent serious environmental degradation and contamination.

Oil Shale

Due to the wide variety of accessory elements associated with oil shales there is a likelihood that mining and processing would result in redistributions of accessory constituents with potentially adverse environmental impact. The high concentration of fluorine in raw oil shale, for example, and its identification in retorted shale, retorted shale leachates, particulates, and ground waters indicate a particular problem to future mining and processing operations. Natural ground waters in some oil shale areas are already known to exceed public health standards for fluorine as well as other elements, such as arsenic, iron, manganese, mercury, and sulfur. Without special mitigating measures, mining and processing of oil shale could aggravate the problems of ground-water contamination.

Because most of the trace elements in oil shale are retained in the retorted shale after processing, a major adverse environmental impact could result from the redistribution of accessory elements through solubilization and resuspension of retorted shale. Of special concern is the large volume of retorted shale that is expected to be generated in a developed industry, as much as a million or more tons per day. The potential for adverse impacts is increased by the fact that retorted shale has a higher porosity than raw shale. Unless waste-pile surfaces are stabilized, this high porosity, in combination with the vast quantities of waste, might permit profound wind erosion and extensive leaching of accessory elements to ground and surface waters. Among the elements of concern in the retorted shale are arsenic, beryllium, cadmium, chromium, cobalt, fluorine, lead, lithium, manganese, molybdenum, nickel, vanadium, and zinc. The mobility of these elements and organic residues with time is a major unanswered question.

The gases produced during retorting and in scrubber wastes also may contain accessory elements that would be redistributed locally and regionally. Although little information is presently available on the composition of off-gases, it seems likely that fluorine, sulfur, arsenic, and mercury will be present and could pose an environmental hazard.

Limited knowledge of accessory element compositions and redistribution mechanisms and pathways makes it difficult to assess rigorously the environmental impacts of oil shale exploitation. But the potential exists for environmental contamination from mining and processing of oil shale. This must be assessed in research and monitoring programs, and to minimize environmental impacts, precautions will need to be taken at all stages of mining, retorting, and waste disposal.

Uranium

The potential escape of radioactive elements to the environment is the principal concern in considering the redistribution of accessory constituents in uranium ores. The average radium content of measured tailings is 700 picocuries per gram, about the same as feed ore. But after mining and milling, radionuclides are more accessible to plants and animals because of exposure of finely ground tailings on surfaces of waste dumps. Exposure can come from wind-blown dust carrying thorium-232 and radium-226, inhalation of radon-222 (radon gas), gamma radiation, or contamination of ground waters. Stabilization of tailings is therefore required. A tailings cover of clay of about 5 feet can attenuate the exposure by an estimated 80 percent. The disposition of tailings is a problem that will increase with expanded mining and milling of uranium ores. The nature of the problem will not change but the the magnitude will. Health effects can be estimated in terms of curie exposure and the population at risk.

Control and management of tailings piles were inadequate at some uranium mills in the past. An EPA survey of 20 inactive mills found excessive radiation within short distances of old tailings piles. Dispersion was due to wind. Some old tailings piles have contaminated streams with radium-226, as well as selenium and vanadium, to the extent that water quality does not meet standards for irrigation or livestock watering.

Phosphates

A number of accessory elements are mobilized in the mining and processing of phosphate ores but two, namely fluorine and uranium, have possible deleterious impacts on the environment and are thus of special concern. During mining, uranium and fluorine contained in the phosphate rock matrix are generally not mobilized, except in the form of airborne particulate emissions. But uranium-decay products do occur in spoil piles where leach-zone rock and overburden are commingled in mining operations, and where there is a potential emanation of radon gas. Mine waste water, which may be discharged into surrounding streams, is a potential escape route of undesirable elements into the environment, but generally these waste waters are cleaned before discharge, as required by state and EPA regulations. Most of the uranium losses occur in the slimes and sand tailings and are of concern because they are commonly used in land reclamation. These wastes can be isolated by capping with a sufficient thickness of overburden, which helps reduce surface radon emanations, but in older mining areas, where clay slimes were merely discarded, the presence of uranium and other radioactive materials near the surface may be an environmental hazard.

The chemical processing of phosphate ores offers the greatest potential for redistribution of accessory elements and compounds. Acidulation processes completely dissolve the apatite host minerals, and accessory elements and compounds are mobilized. Fluorine finds its way into stack emissions, process water, and waste products. Emission standards require the scrubbing of stack gases to minimize fluorine escape into the atmosphere. Yet, some leakage into the environment still occurs. Process water likewise contains fluorine and must be controlled to prevent loss of fluorine into the surrounding subsurface-water environment. Solid fluorides in waste products are generally contained within the processing and storage-pond systems, although storage-pond water does provide an escape route for fluorine emissions to the atmosphere. If pond waters must be released they are first treated to meet EPA standards so as to minimize any potential contamination of surface and ground waters.

Most of the heavy metals found in phosphate ores are retained in wet-process phosphate fertilizers and eventually find their way into the soils, where they may be absorbed by soil minerals, taken up by plants or leached into surface or ground waters. However, the concentrations of heavy metals in fertilizers are very low and may not result in any increased concentration in plants. The uptake of uranium and radium contained in fertilizers is likewise believed to be low but worthy of mention for environmental monitoring.

Alumina

Because the data base on accessory elements in non-bauxitic materials is so limited it is not possible to provide a confident assessment of the potential environmental impact of mining and processing activities. However, some data are available. In the Alumet process for treating alunite the slurry water is known to be mildly alkaline, but will not contain significant concentrations of heavy metals or toxicants in solution. But off-gases from roasting of the alunite ore, if not cleaned, might contain enough sulfur dioxide and particulate emissions to cause some environmental degradation. There might also be some leaching of pyrite from alunite waste piles.

In any processing of dawsonitic shales for alumina it can be expected that accessory element redistribution problems will be essentially those of processing oil shales for their oil content. There will be large volumes of waste to be disposed of which might be leached of accessory constituents such as arsenic, fluorine and certain sulfides, and in turn contaminate ground-water supplies. Blowing dust from fine particles in waste piles could also be a problem. In addition, arsenic, fluorine and other elements might accumulate in retort waters and find their way into the environment.

Anorthosites and nepheline syenites are not mined in the United States today for their alumina content and little is known about the possible fate of accessory elements in any processing scheme. There are extremely limited data on which to base any assessment of the environmental impact of mining and processing. However, should these rocks be processed for alumina, there could be some redistribution of elements as a result of sintering, leaching, desilication, calcination, and evaporation. Not enough is known at present to predict what redistributions of accessory elements might occur.

Potential for Byproduct Recovery

Coal

The potential for byproduct recovery of accessory elements found in coals would appear to be substantial. By virtue of the large volumes of coal that are processed and burned, the quantities of accessory elements that might be recovered become significant, even though the elements may occur only in minor or trace amounts in the raw coal. Some coal-processing wastes may contain more than 2.5 times the trace-element concentration of the raw coal and could provide feed for subsequent upgrading and possible recovery. The economic recovery of accessory elements from coal-preparation-plant refuse is improved to the extent the production of the coal has borne the total mining and initial preparation costs. As market prices rise the refuse from fine-cleaning may warrant special attention for recovery of accessory elements. Additional crushing would not be necessary and, in general, traditional concentration and separation techniques could be employed to produce a final product. Alternatively, leaching might permit the recovery of heavy-metal ions from coal-preparation wastes by hydrometallurgical techniques, such as precipitation, adsorption, ion exchange and solvent extraction.

Ash and combustion wastes from coal-fired power plants and the wastes resulting from coal-conversion processes all contain significant quantities of accessory elements and might have some potential for byproduct recovery. However, data are presently insufficient to make other than speculative judgments about this potential.

Oil Shale

The opportunities for recovering byproducts in the processing of oil shale are difficult to assess due to the paucity of basic data on form, concentration, and process for potential product development. The most attractive opportunities lie in the recovery of aluminum from dawsonite and soda ash from nahcolite. These accessory minerals are widely associated with oil shale in the Piceance Creek Basin and might be economically recovered in large-scale oil shale operations.

Uranium

Byproduct elements associated with uranium ores all have sources of supply much greater than that involved with production of uranium oxide. Accessory elements in uranium ores are incidental and are of economic importance only insofar as they affect the cost of a particular operation. However, there is a potential for recovery of certain elements. Some Utah and Arizona uranium ores contain .15 to 2.0 percent copper and trace amounts of silver. The copper can be recovered by flotation of sulfides and concentration of solubilized copper from effluents from uranium ion-exchange or solvent-extraction processes.

Molybdenum can be recovered and has been marketed in limited amounts as a calcium molybdate or ammonium phosphomolybdenate containing 40 to 50 percent molybdenum. Recovery of molybdenum is significant only as an environmental or purity consideration. Other elements, such as rhenium, scandium, selenium, thorium-232, and vanadium, could be recovered but there is no economic incentive to do so at this time.

Phosphate

Byproduct production of accessory elements in phosphate chemical plants has been limited by virtue of the costliness of recovery methods. Even though certain metals and rare earths are in solution in the phosphoric acid process it has not been economic to recover them. However, the large volumes of phosphates treated annually in fertilizer manufacture might make byproduct recovery feasible for some elements, for example, the rare earths. Fluorine, which is present in significant quantities in the production of phosphoric acid, must be controlled to meet EPA emission standards. It can be readily recovered as a byproduct of phosphoric acid and elemental phosphorus production but at present there is no economic incentive to do so.

Of greater attractiveness today is the potential for byproduct recovery of uranium, which is present in phosphate ores in amounts averaging .01 percent. Despite this trace amount of uranium in phosphate ores, the total quantities of phosphoric acid produced each year, together with increasing prices for uranium oxide, make uranium recovery of economic interest. Some large phosphoric acid producers currently recover byproduct uranium and several others have announced their intentions of constructing facilities to recover this byproduct uranium. Uranium might also be recovered in the production of elemental phosphorus. The projections of the U.S. Department of Energy (DOE) and others suggest than as much as 4,000 tons or more of uranium oxide will be recovered each year by the phosphate industry.

Of lesser interest is the byproduct potential in the production of elemental phosphorus. Slag from phosphorus furnaces has some potential as an aggregate material. Ferrophosphorus is at present a commercially viable though limited byproduct from the production of elemental phosphorus, and some precipitator dust has been sold as a byproduct for its phosphorus pentoxide and potash fertilizer values. Vanadium, chromium, germanium, and gallium may have some very limited potential as byproducts of elemental phosphorus production, but there is little economic incentive to recover these products at present.

Alumina

The potential for byproduct recovery of elements associated with processing alumina ores is not very high. Silica from the treating of high-alumina clays might be recovered and find use as a filler for newsprint and rubber, and if the titania content could be concentrated it might be a source of pigment-grade titanium oxide.

Potassium sulfate is a probable coproduct of the Alumet process in treating alunite ores and the production of sulfuric acid is a potential byproduct of all the schemes considered in processing alunite. In any processing of dawsonitic oil shales for alumina it is likely that nahcolite would be recovered as a coproduct for the production of soda ash. Retorted shale might have some potential use in lightweight aggregates, portland cement, brick, road construction materials, and glass and glass ceramics. Potassium could be a potential byproduct of processing anorthosites, and both sodium and potassium byproducts of nepheline syenites. However, there is at present no incentive to recover byproducts from non-bauxitic rocks and the potential for byproduct recovery is discussed only insofar as large-scale mining and processing might be undertaken at some future date and make byproduct recovery possible.

Technological Impact on Future Mining and Processing

Coal

The technologies in use today are expected by industry to remain in use for many years in the mining and processing of much of our coal output. The scale of individual surface-mining operations in western coal seams may be nearing a peak. No radically new types of equipment are under development. This does not imply that mining technology is satisfactory. No mechanical mining methods are available for the thick deep seams which will have to be extracted by underground-mining methods. Until such systems are devised it is uncertain how future accessory element redistribution from such deposits will be affected.

Strip-mining practices in both western and eastern deposits will be changed by the Surface Mining Control and Reclamation Act of 1977. Enforcement of the Act should result in a reduction of the impacts of accessory element redistribution per ton of coal mined, since it disqualifies from mining certain types of deposits where environmental impacts are difficult or nearly impossible to control economically.

Underground mining in the eastern thinner seam deposits will require new mining systems and equipment in order to help reverse the decline in productivity that has occurred in the past 10 years. Such systems have not yet been developed. Attempts to introduce longwall mining in place of room-and-pillar methods have met with limited success. On balance, it is not likely that new problems associated with accessory element redistribution, other than those resulting from increased production, will arise.

In the processing of mined coal, one can expect an increase in the amount of coal that is beneficiated in order to reduce emission of pollutants during utilization. This will result in production of increased quantities of solid wastes per ton mined, from which the escape of accessory elements must be prevented. New higher-cost and more efficient technologies for beneficiation may be developed but existing processes will probably continue to dominate the industry for many years.

Direct coal combustion will continue to be the major use for coal for at least the next 20 years. If national energy policies are implemented to the degree contemplated, the combustion of coal will more than double in the next 10 years. Requirements to prevent environmental contamination will almost surely result in attempts to improve coal-cleaning processes, coal-burning systems, and disposal of wastes, and these in turn will affect the redistribution of accessory constituents. For example, control of sulfur oxides by using stack scrubbers and throwaway lime or limestone processes will create very large tonnages of solid wastes, from which the potential for accessory element redistribution into the biosphere is very great. Alternatively, sulfur oxide control might be achieved by the use of fluid-bed combustion but this also creates a new set of problems with respect to environmental controls and possible accessory element redistribution.

Coal-conversion processes to convert coal to liquid or gaseous fuels, once they become commercial, will affect the redistribution of accessory elements and compounds. These processes create solid, liquid, and gaseous residues that are chemically different from those that are generated by direct combustion and will generally require different environmental control practices, if redistribution of accessory elements is to be minimized. The exact chemical nature of these substances and methods required to prevent their dissemination into the environment will not be known until we have had, at the very least, substantial experience with pilot-plant design and operation.

In situ coal gasification presents some unique technical environmental problems and possibly increases the mobility of accessory elements at considerable depths in the earth. Ground waters could become enriched and perhaps polluted with certain elements. But one can only speculate about the changes that might occur since there is no information on the special environmental problems and effects that will be created by _in situ_ gasification, a process that takes place under conditions that are extremely difficult to control and are highly site-specific.

Oil Shale

A number of different above- and belowground processes have been developed or are being developed to extract oil from oil shale, but the accessory element contents of products and residuals as a function of technology type and process variables are only now becoming available. It is thus possible to assess the relationships of technology to the redistribution of accessory elements only in a general way. General distributions of accessory elements can be predicted but the mechanisms and pathways of redistribution need to be better understood. Aboveground retorting is now quite refined but belowground retorting remains under development.

Uranium

Substantial changes in extractive metallurgical processing of uranium ores are not likely in the next 25 years, especially changes that might affect the production of accessory elements or cause environmental concerns. A possible exception is *in situ* leaching of uranium ores, which will cause mobilization and possible escape of uranium and some associated elements from the leach field. Present knowledge of the fate of accessory elements and compounds in the *in situ* leaching of uranium ores is poorly known.

Except for radioactive constituents, there is some similarity in the accessory element content of uranium and copper ores. The wide technological base for processing copper ores suggests that environmental concerns and possible byproduct production as uranium mining increases should pose no new questions.

Phosphates

It is likely that the production of phosphates over the next 25 years will use existing mining, beneficiation, and processing technologies, and in general no major new problems in the redistribution of accessory elements and compounds should arise. Exceptions to this might develop if new technologies are devised to recover offshore phosphate deposits. Any new technology could spawn new problems in the redistribution of accessory elements and compounds. Processes for recovery of uranium from phosphate ores are well developed. However, sustained production of byproduct uranium could result in new technical requirements, waste products, and conditions of disposal that could bring additional problems of redistribution.

Alumina

The technological impact of processing non-bauxitic sources of alumina can be assessed only in a speculative way in the absence of any commercial production from these sources. Acid processing of high-alumina clays has been tested in pilot plants and some information is available on the fate of accessory elements mobilized in these operations. Alunite has been processed commercially in other countries for its alumina content and some data are available on the effects of caustic-leach and acid-leach processes on the redistribution of accessory elements.

Techniques for processing dawsonitic oil shales have been developed but it is too early to evaluate the effects of these techniques, either in assessing byproduct recovery potential or environmental impact of redistributing accessory elements. Virtually nothing is known about processing anorthosites and nepheline syenites other than the probable use of sintering and leaching methods as a basis for recovering alumina. If non-bauxitic aluminum resources are exploited in the future it is likely that some new processing technologies may be required, but at present no new methods of treating these materials are known to be under development.

REDISTRIBUTION OF ACCESSORY ELEMENTS AND COMPOUNDS FROM MINING, PROCESSING, AND UTILIZATION OF COAL

SUMMARY

Coal will be used in increasing amounts over the next quarter century, not only in coal-fired power plants but for metallurgical and industrial processes and in new products or synthetic fuels. The increased use of coal may result in significant environmental impacts through the redistribution of accessory elements and compounds if proper control measures are not taken. At the same time, however, there will be opportunities for recovery of potentially useful and economically recoverable elements present in accessory compounds and minerals found in coal. The principal interest is in the potentially harmful and economically useful constituents. It is estimated, for example, that a coal-conversion plant will use 8 million tons of coal per year and, in the process, generate about 2 million tons of solid wastes and lesser amounts of liquid and airborne wastes. Because coals contain a wide range of potentially hazardous and useful elements, it is desirable to examine the prospects for the redistribution and recovery of such elements.

The chemical reactivity (for example, solubility and volatility) of a coal's accessory elements during the processing and utilization is a function of both the physical and chemical combinations in which the elements occur and of the processes to which the coal is subjected. The total amount of an accessory element in a particular coal is related to a number of complex factors, such as: (1) composition and source of the original peat, clay, and other minerals added during and after peat accumulation, (2) biochemical reactions throughout geologic time, and (3) hydrologic interchange with surrounding rocks. And, finally, the mining technique used to extract the coal will exert an influence on extraneous elements and impurities. To predict the redistribution (and recovery) potential for the large number of elements found in coal (for example, Ca, Fe, As, Se, Sb, F, Pb, Zn, and S), many of which occur in several different chemical and physical combinations, it is necessary to know their total concentrations and their modes of occurrence (in organic or inorganic compounds, for example).

Within the last few years, data on the distributions and concentrations of accessory elements in different coals from different areas have become more extensive. Useful as they are, however, these

data are far from sufficient for the accurate prediction and mapping of mean concentrations in individual coal basins and beds, because of the wide variances in distribution and the relatively small number of samples analyzed. Nevertheless, there are suites of accessory elements that can be consistently identified in certain coals. For some of the major coal seams now being mined, patterns of occurrence are beginning to emerge. To date, only As, B, Ba, Sb, and Se are found consistently enriched in whole coals compared to their mean crustal abundances. Generally, the concentrations of accessory elements in individual coals are lower than in the surrounding rock and lower than the mean crustal abundance. A few elements, though, such as zinc and cadmium in the Interior Coal Province of the United States, show local or regional enrichment in the coals, and this is commonly reflected in the surrounding rock formations as well. For the most part, however, mean trace-element concentrations are higher in shales and clays above, below, or within coal beds than they are in the coal. Because of this, coal-preparation methods are designed to remove much of the shale and clay taken in raw-coal mining; conventional coal cleaning can reduce significantly the levels of trace elements that would otherwise be redistributed when the coal is used. Coals so cleaned also considerably reduce ash content.

In coals of the United States' Appalachian Province, much of the pyritic sulfur can be removed at low cost by conventional preparation methods. In many coals of the Eastern Interior Province, however, which contain high levels of finely disseminated pyritic and organic sulfur, conventional coal-cleaning methods will not bring the washed coal to standards (1.2 pounds of sulfur, or less, per million Btu produced) proposed by the U.S. Environmental Protection Agency (EPA). Some authorities infer from this that trace elements not in mineral form in raw coals may not be removable by conventional cleaning. With the possible exception of sulfur, little is known about the forms and combinations and the frequency distribution of accessory elements in coal.

Information about the accessory element composition of coal-preparation-plant wastes is scant, even though some 100 million tons of waste are produced annually in the preparation of coal. The mean ash content of raw coal has increased in recent years because of the increased use of automated mining techniques, increased strip and auger mining, and the general decline in the availability of higher-quality metallurgical-grade coals. Nonetheless, it is clear that the fine discharge from conventional coal-preparation plants comes primarily from the shales and clay partings of the mine roof or bottom that are mined with the coal. There is also evidence that concentrations of many of the nonpyritic trace elements, such as boron, antimony, and vanadium, thought to be associated with organic rather than mineral matter in coal, are relatively low.

Studies of the accessory constituent composition of coal-cleaning wastes show that some elements (for example, Cd, Cr, Cu, F, Hg, Ni, Pb, and Zn) are more concentrated, by factors of 3 to 10, in preparation-plant wastes than in the raw coal. Research is in progress on the desulfurization of boiler fuels to the deeper cleaning levels common in preparing metallurgical coal. Research is also being conducted on new methods of physical and chemical separation. Little is known about the possibilities for their use in the removal of other accessory elements from coal. Estimates of their efficacy for this are complicated by the fact that conventional coal-cleaning wastes remain incompletely characterized.

Large increases in the use of coal as a fuel for boilers and fluidized-bed combustion units will aggravate the existing problems of disposing of wastes such as ash, fly ash, slag, and products of stack-gas scrubbing. Thus the control of trace metals and accessory elements other than sulfur in stack gases probably will be required. Undesirable elements identified in the stack emissions to date include Hg, Se, F, S, B, Cr, V, and very small amounts of radioactive nuclides. We must learn much more about the health effects of such elements and their effects on plants, animals, and humans. This is especially true for chronic or continuous low-level exposure. The accumulation of certain elements in plants and damage to susceptible grasses and conifers has been demonstrated in the western United States, although some elements have been found to be beneficial to certain types of plants under certain conditions.

Sulfur, phosphorus, and many other accessory elements are beneficial or essential to plant and animal nutrition. Most notable among the elements found in stack emissions from coal-fired boilers are sulfur and fluorine, which can be transported long distances in the atmosphere and deposited as acid rain (dilute sulfuric and hydrofluoric acids). Many elements and organic compounds are concentrated on particles too small to be trapped by conventional stack-gas cleaning equipment, mainly wet scrubbers and electrostatic precipitators. Recent studies of the control of particulate and gaseous emissions, however, indicate that these problems may be solved through the combination of fabric filters, temperature control, and improved stack-gas scrubbing, and these technologies promise more efficient control of both particulate and gaseous emissions of accessory elements than has been achieved to date.

Concern over emissions and effluents from proposed coal-conversion plants has stimulated much research. Some pilot and demonstration plants are being constructed and tested in the United States; the basic chemical reactions that occur in these processes are known. Because the reactions take place in confined vessels, coal-conversion processes control emissions more effectively than current coal-utilization practices. Nevertheless, health effects of liquid effluents, gaseous emissions, and byproducts are incompletely known and need careful study. It is known that some tars produced from coal-gasification and liquefaction processes contain relatively high concentrations of lead, arsenic, and titanium, as well as organic compounds known to be carcinogens. Thus, there is a need for thorough study of accessory element concentrations in byproduct streams as well as in wastes. Moreover, commercial-scale application of control equipment will be needed to determine reliably the disposition of accessory elements and compounds emanating from the proposed coal-conversion plants.

If predictions concerning the increased number of coal-fired, electricity-producing plants and the development of coal-conversion processes are correct, the late 1980s will see the production of unprecedented quantities of solid wastes, which will require disposal. Successful commercial-scale production of synthetic gas and oil from coal may depend critically on the economic and environmentally acceptable disposal of wastes, and perhaps on byproduct recovery. Solid-waste products from pilot-scale coal-gasification and liquefaction processes in the United States are now available for chemical and mineralogical characterization. It is clear that solid residues will be the major sink for many accessory elements and that these wastes will contain mineral species not originally present in the raw coal. After disposal, these materials may undergo different chemical reactions from those in cleaning and combustion wastes.

The solubility of accessory elements in solid wastes is probably as important in their redistribution in the environment as is their total concentration. Solubility depends upon their chemical form, the pH and Eh (oxidation potential) of interstitial waters, and the physical properties (such as particle size and internal surface area) of the materials containing the elements. The mobility of a compound or ion in the environment depends on many factors. These include climate, local ground-water conditions, adsorption capacity of the system (cation and anion exchange capacity of clays and organic material), competing ions in solution, and the action of organic matter alone or in conjunction with microorganisms in forming organometallic compounds. Because of the complexity of the interactions responsible for the solubility, mobility, and attenuation of accessory elements from coal wastes, and because of the many different elements and compounds involved, much research remains to be done before an evaluation of any beneficial or deleterious environmental effects can be made. Additional baseline studies concerned with, for example, the relatively unspoiled landscape and biosphere in the western coal areas of the United States will be required before significant production develops. Likewise, detailed studies of environmental effects in areas where coal has been intensively mined and burned during the past century need to be made.

Laboratory solubility studies indicate a potential for contamination of surface and ground water by the leaching of piled or buried coal wastes. For example, in laboratory leachates produced under a variety of pH and Eh conditions from gasification ash, the concentrations of B, Ca, K, Mn, NH_4, Pb, SO_4, and Sb exceed current EPA water quality levels. If present in ground water, such leachates may be diluted only slightly because of limited flow and mixing. Fly ash, which is usually transported as a water slurry and stored in ponds or buried in strip-mine pits along with bottom ash, has been found to be sufficiently soluble to yield leachates that exceed acceptable water quality criteria for As, B, Ba, Cd, Cr, Mn, and Se. These elements were identified in untreated and recirculated ash sluice water. In less acid leachates from western coal spoils, Mn, Ca, Mg, Na, and NO_3^- are strongly enriched.

Various methods for the environmentally safe disposal of coal wastes are being considered and tested. One method that has received considerable attention but has undergone insufficient testing is disposal in surface or underground mines. However, the disposal of alkaline conversion wastes in surface-mine pits, which may give rise to acid mine drainage, is likely to increase the solubility and mobility of many accessory elements. It has been shown that adsorption of the cationic metals Pb, Cd, Zn, Cu, Hg, and Cr^{3+} by earth materials increases as the pH increases, while adsorption of the anionic metals Cr^{4+}, As, and Se decreases as the pH increases. Thus, pH has a significant effect on the capacity of certain materials, such as clay minerals, to attenuate or mitigate the migration of accessory elements.

In addition to knowledge about the concentrations and solubilities of accessory elements in whole coal, coal wastes, and coal byproducts, new information is urgently needed on their beneficial and deleterious effects under various laboratory and field conditions. Inorganic constituents and water-soluble organic compounds such as humic and fulvic acids may occur in the effluent from coal wastes that contain appreciable amounts of processed organic matter, such as coal-liquefaction residues. Preliminary results indicate that there may be some toxic products from coal-conversion leachates and extracts, but how they are redistributed in nature has not yet been determined. Nor has consideration yet been given to possible beneficial effects that might accrue from the redistribution of these leachates and extracts.

No diseases have been identified as resulting from coal-related, inorganic trace-element pollution. However, this does not mitigate concerns arising from a large increase in coal utilization and from those effects resulting directly from processing and combustion or indirectly from land disturbance due to mining. Obviously, care must be taken not to indict arbitrarily all accessory elements contained in coal and coal-related materials. Many are necessary to life and are known to be beneficial to plants, animals, and humans. Research should be designed to reveal both the beneficial and the deleterious aspects of accessory element redistribution.

The potential for recovery of economically valuable byproducts from coal waste and processed coal products needs considerable attention. Accessory element recovery from coal-preparation-plant refuse may be economically attractive because recovery of the coal itself removes the mining and most of the preparation costs. A logical feed stream for such a recovery process would be the refuse product from fine-cleaning sections. This would obviate the need for major additional crushing. It is possible that extraction and use of the accessory constituents may significantly reduce both the potentially deleterious effects and the costs of coal-waste disposal. The selection of those coal beds that contain high concentrations of elements for recovery, for example zinc- and cadmium-containing sphalerite in coal beds of the Interior U.S. Coal Province, would enhance the prospects of success. Byproduct recovery processes are successful in other industries.

There are difficulties in making an economic evaluation of recovery processes for accessory minerals at this time. The range in values reported for accessory elements in various coals is often 1 or 2 orders of magnitude. The amounts and distribution of accessory elements are incompletely known because of the relatively small number of coal samples analyzed, and the problem of what is a statistically meaningful sample. Further, it is not likely that total concentrations of particular accessory elements in a whole coal truly represent the amounts ending up in a particular waste stream, for example, ash, and therefore such estimates may not be representative of the actual amounts recoverable from that stream.

The problems in making unqualified economic predictions for byproduct recovery from coal are compounded by lack of information in the following areas:

1. Except for sulfur, published data provide little basis for the quantification of the relation between raw-coal and clean-coal analyses. Existing studies do not distinguish among the levels of cleaning, while costs related to cleaning level may vary substantially.
2. Washability characteristics related to separation of most accessory elements from the coal do not exist for specified size ranges and may not be complete enough to project the potentials of most beds of run-of-mine coal.
3. Because raw coals are variable in composition, there can be no standard flowsheet for coal-cleaning plants capable of treating all coals of current interest.
4. There is no way to compare byproduct values for different coals that have different crushing and washability properties except on a specific cleaning-plant basis; thus, useful generalizations cannot now be made.
5. Preliminary studies give very little information about the relation of refuse handling to costs for a specific coal. Little information exists on the costs of mine waste reclamation and potential tradeoffs.
6. Very little information is available on the utilization or disposal costs of very fine coal particles that generally make up 20 to 30 percent of cleaning-plant wastes.

Thus, on the basis of present information, the data on trace and minor constituents in coal are too meager and variable to predict accurately the commercial future of recovering these constituents or to predict the environmental impact of conventional coal utilization. Nevertheless, it is apparent that, even with the added expense of coal cleaning and stack-gas scrubbing, coal will replace petroleum liquids and gas as fuel for large-scale boilers because of its much greater abundance and relatively lower cost than other fossil fuels. Future problems created by the increased amount of waste associated with coal are likely to be severe but may be diminished by efforts to recover minerals from waste.

INTRODUCTION

This report evaluates available information about the kinds and amounts of accessory constituents in coal and examines, in the light of the expected increase in coal use and the introduction of new methods for coal processing, the potential for their redistribution in the environment and for byproduct recovery. The study includes both current and proposed coal-mining, cleaning, combustion, and conversion processes. Many of these processes produce solid, liquid, and gaseous wastes or byproducts containing concentrations of accessory elements significantly higher than those in the original coal. Consideration is also given to future problems resulting from the redistribution of accessory elements originally in coal and to related research needs.

Accessory elements in coal are classified according to (1) whether they are indigenous in the coal, (2) occur in associated rock partings, or (3) derive from the roof and floor rocks. The contributions from (2) and (3) depend largely on the type and efficiency of the mining operation. Indigenous accessory elements may occur in either organic or inorganic combinations, and may be primary (syngenetic) or secondary (epigenetic) in origin. Primary inorganic minerals such as clay and quartz were intermixed with the coal material by wind or water action at the time of peat accumulation. Secondary inorganic minerals formed after burial of the coal through the filling of fissures, fractures, or other voids by minerals such as pyrite, precipitated from dissolved salts transported by ground water. The inclusion of fragments of roof and floor rocks in the mined product have an important bearing on the accessory element composition of the material shipped and used as coal in many areas.

Organic remains of plant or peat material in coal have been classified by appearance, especially by their degree of brightness or dullness. These petrographic constituents of coal are called durain (dull), vitrain (bright), clarain (intermediate), and fusain ("mineral charcoal"); these differences in appearance may be associated with differences in inorganic or mineral composition within the same bed and locality.

The chemical and physical character of the organic matter in peat and low-rank coals can have a significant effect on accessory element composition. Functional groups (-OH and -COOH) can bond Ca, Mg, Na, K, and Fe, for example, to form salts of acids, or they can form chelated compounds with heavy metals such as Cu, Ni, and Ge. These coals have properties similar to ion-exchange resins or some clay minerals and can be characterized by an ion-exchange capacity. Such accessory elements are sometimes referred to as organic, but they are more easily removed and have considerably different chemical reactivities than those originally contained within the coal itself. It is also likely that many chemical properties (solubility, volatility, etc.) of organically associated elements are significantly different from inorganically combined elements.

The origins of accessory elements in coal are complex, variable, and of great significance in terms of accessory element reactivity, removal, and redistribution during coal processing and utilization. Indeed, the fundamental nature of coal is of very practical interest and urgently requires a great deal of new research. A recent article reviewing research being conducted in this subject has been published by Ensminger (1977).

COAL EXTRACTION

Coal is extracted by surface- (strip) and underground-mining methods, each of which is comprised of several types. These methods and the factors affecting their use were recently summarized (Argonne National Laboratory 1977) and are described in numerous texts and articles.

Coal mining has been an important cause of the redistribution of accessory elements in the Appalachian and Eastern Interior Coal Regions for at least two reasons. First, if strip-mined areas are left untreated, the redistributed layers of overburden can become extremely acid (pH 2 to 4) due to subsequent leaching and weathering of pyrite (FeS). In a later section of this report, it is shown that low pH values are conducive to high solubility and mobility of certain accessory elements, for example, Co, Cu, Cd, Cr, and Zn.

Second, drainage from strip and underground coal mines in the eastern half of the United States can be highly acidic. Acid mine drainage (AMD) resulting from the oxidation of pyrite may contain concentrations of iron and sulfate greater than 1,000 parts per million; Al, Mn, and Zn can exceed 100 parts per million. Other elements frequently contained in AMD includes As, Cd, Cr, Co, Cu, Pb, N, Se (Appalachian Regional Commission 1969, and Colgate et al. 1973). Drainage from abandoned underground mines is the greatest single source of acid mine water and probably the most difficult to control (Argonne National Laboratory 1977). Moreover, ground-water resources may be adversely affected by acid mine water when spoils are used to refill a mine. Highly mineralized leachates can be generated by percolation of water through the fill and into aquifers.

Information concerning the effect of new practices (AMD neutralization, grading, revegetation, etc.) on reducing or preventing the redistribution of accessory elements resulting from coal extraction is virtually nonexistent. However, as new reclamation laws become effective, future AMD problems should be significantly reduced.

Because they contain little pyrite, western coals do not produce AMD. Rather the drainage is classified as hard or saline depending upon whether calcium and magnesium or sodium ions are predominant. Relatively high salt concentrations already present in some western surface waters tend to reduce the adverse effects from acid mine drainage.

COMPOSITION OF COAL AND COAL-RELATED MINERALS AND ROCKS

Composition of U.S. Coals

During the past 10 years there has been renewed study of accessory constituents in coal. Combined with previous studies, presently available information gives a fairly comprehensive view of the kinds and amounts of accessory elements in coals of the United States. (See Table 1.1; a more extensive treatment, based on coal province, is given in Appendix A, Tables A1.1 through A1.3 and A1.6 through A1.9.)

In the following sections, brief summaries of the variations in coal composition are given for the major coal-producing provinces in the United States (Swanson et al. 1976, Hatch and Swanson 1977, and Medlin 1977). For a brief description of province location by state see Table 1.2.

Pennsylvania Anthracite

Comparison of the geometric means of elements in 53 Pennsylvania anthracite samples with the mean values for shale (Table A1.1) shows that the amounts of Zn, Ba, and V are less than one-fifth as large in the anthracite as in shale; and the amounts of Ca, Mg, Na, K, Fe, Mn, F, and B are less than one-tenth as large as in shale. Only selenium is enriched in the anthracite, where the amount of selenium is about 5

TABLE 1.1 Composition of U.S. Coal*

Element	All Coal (799 samples)	Anthracite (53 samples)	Bituminous (508 samples)	Sub-bituminous (183 samples)	Lignite (54 samples)	Average Shale
Percent						
Si	2.6	2.7	2.6	2.0	4.9	7.3
Al	1.4	2.0	1.4	1.0	1.6	8.0
Ca	.54	.07	.33	.78	1.2	2.21
Mg	.12	.06	.08	.18	.31	2.55
Na	.06	.05	.04	.10	.21	.96
K	.18	.24	.21	.06	.20	2.66
Fe	1.6	.44	2.2	.52	2.0	4.72
Mn	.01	.002	.01	.006	.015	.085
Ti	.08	.15	.08	.05	.12	.46
Parts per million (ppm)						
As	15	6	25	3	6	13
Cd	1.3	.3	1.6	.2	1.0	.3
Cu	19	27	22	10	20	45
F	74	61	77	63	94	740
Hg	.18	.15	.20	.12	.16	.4
Li	20	33	23	7	19	66
Pb	16	10	22	5	14	20
Sb	1.1	.9	1.4	.7	.7	1.5
Se	4.1	3.5	4.6	1.3	5.3	.6
Th	4.7	5.4	5.0	3.3	6.3	12
U	1.8	1.5	1.9	1.3	2.5	3.7
Zn	39	16	53	19	30	85
B	50	10	50	70	100	100
Ba	150	100	100	300	300	580
Be	2	1.5	2	.7	2	3.0
Co	7	7	7	2	5	19
Cr	15	20	15	7	20	90
Cs	7	7	7	3	7	19
Mo	3	2	3	1.5	2	2.6
Nb	3	3	3	5	5	11
Ni	15	20	20	5	15	68
Sc	3	5	3	2	5	13
Sr	100	100	100	100	300	300
V	20	20	20	15	30	130
Y	10	10	10	5	15	26
Tb	1	1	1	.5	1.5	2.6
Zr	30	50	30	20	50	160

*Average amounts of 36 elements in coal samples and in different ranks of coal, presented on whole-coal basis. For comparison, average amounts in shale are also listed.

SOURCE: Swanson et al. (1976), Turekian and Wedepohl (1961).

TABLE 1.2 Distribution of Coals in the United States by Province

States						
Appalachian	Interior	Northern Great Plains	Rocky Mountain	Pacific	Gulf	Alaska
Pennsylvania Ohio Virginia West Virginia Eastern Kentucky Alabama Tennessee	Eastern Coal region: Indiana Illinois Western Kentucky Western Coal region: Oklahoma Missouri Kansas Arkansas	North and South Dakota Montana Northeastern Wyoming	Many distinct basins of different geological history in Southwestern Wyoming, Colorado, Utah, New Mexico, and Arizona	Washington Oregon California	Parts of Arkansas Texas Louisiana Mississippi Western Alabama	Alaska

SOURCE: Ensminger (1977).

times larger than the average in shale. The amounts of the 24 other elements reported are similar to those for shale.

Appalachian Province

Comparison of the geometric means for the accessory elements in 331 coal samples (Table A1.2) from this province with those of shale indicates that the amounts of Al, Fe, Ti, F, Ba, and V are less by a factor of more than 5; the amounts of Ca, Mg, Na, and K are less by a factor of more than 10. Selenium is enriched in the coal by a factor of more than 5. The amounts of the 25 other elements reported are very similar to those in the average shale.

Interior Province

Comparison of the geometric mean of elements of 155 Interior Province coal samples (Table A1.3) with average amounts in shale shows the amounts of Al, Mn, Ti, Li, Ba, Cr, Sr, and V in coal are less by a factor of more than 5; the Mg, Na, K, F, and Zr contents are less by a factor of more than 10 than in the shale. Selenium abundance in the coal is greater by a factor of more than 5; and cadmium is enriched in the coal by a factor of more than 10. The amounts of the 21 other elements reported are similar to those in shale (also see Leonard et al. 1965).

Work by Hatch et al. (1976a,b) on coal from the Interior Province provides more detailed information on the average zinc and cadmium concentrations in whole coal from southeastern Iowa, Missouri, and southeastern Kansas. The zinc concentration (whole-coal basis), resulting from the sphalerite (ZnS) in these coals, ranges from 14.4 parts per million (ppm) to 18,800 parts per million (for complete data, see Table A1.4). These are some of the highest zinc values ever reported in coal. Cadmium content of the same coal samples ranges from .2 to 60.2 ppm. Hatch's work also revealed high concentrations of Sb (300 ppm), Co (700 ppm), Cu (520 ppm), Pb (2,770 ppm), Mo (1,000 ppm), Ni (1,500 ppm), and Ag (15 ppm) on an ash basis. The anomalously high zinc values in Interior Province coals were first noted by Zubovic (1966).

Detailed work by Hatch et al. (1976b) on zinc and cadmium in Illinois coals revealed the same type of mineralization as described above. Extended work involving several groups within the U.S. Geological Survey and the Illinois State Geological Survey is under way to understand better the distribution, mode of occurrence, and economic potential of these elements in Illinois coal and coal waste.

In this connection, rather complete chemical data for Illinois coals have been published by Ruch et al. (1976) and Gluskoter et al. (1977). The relatively high zinc and cadmium concentrations in coal from the Interior Province are reflected in the data given in these reports (Table A1.5).

Work by Zubovic (1966) on coal in the Illinois Basin revealed anomalously high concentrations of vanadium and, to a lesser extent, chromium and nickel in the topmost portions of the Kentucky No. 9 coal bed and its correlatives in Illinois and Indiana. Based on subsequent work, Gluskoter et al. (1977) later concluded that U, Mo, V, and Ge are concentrated in the uppermost parts of individual coal beds. Antimony was also more abundant in uppermost benches in four sample sets and in the bottom bench of a fifth sample set.

Gulf Coast Province

Comparison of the amounts of elements in 34 lignite samples (Table A1.6) with those of shale shows the amounts of Mg, K, and F in coal are less by a factor of more than 5. Selenium is enriched in coal by a factor of more than 10. The amounts of the 32 other elements reported are very similar to the average amounts for shales.

Northern Great Plains and Rocky Mountain Provinces

Elemental data for 490 and 295 coal samples from the Northern Great Plains (Table A1.7) and Rocky Mountain Provinces (Table A1.8), respectively, indicate that mean amounts of 35 elements are less in the coal than in average shale. Only selenium is more abundant in the coal than in shale.

A comparison of the amounts of elements in coal from the Rocky Mountain and Northern Great Plains Provinces with the amounts in the Interior Province shows that the Interior Province coals are considerably more enriched in many of the minor and trace elements. It should be noted that the uranium content of coal in the Northern Great Plains and Rocky Mountain coals also is less than the average uranium content of shale. (See comments later in this chapter regarding interpretation of average concentrations.)

Alaskan Province

Comparison of the geometric means of elements in these coals (Table A1.9) with those in the average shale indicates that the amounts of Al, Ti, F, Li, Cr, Ni, and Zr in coal are less by a factor of more than 5, and that Na, K, Fe, and Mn are less by a factor of more than 10. Mercury is apparently enriched in the coal by a factor of more than 10, but coal-sample contamination is suspected. The amounts of the 24 other elements reported are similar to those in shales.

Composition of Coal-Related Minerals and Rocks

The following is a summary of the amounts of accessory elements in roof rock, coal partings, and floor rock associated with coals of the United States (Medlin 1977; see Tables A1.10 through A1.13).

1. The amounts of Ag, Ba, Be, Cd, Co, Cu Ge, Hg, Mo, Ni, Pb, Sb, Se, and Sr are greater in the partings of Eastern Interior coals than (a) in floor-rock samples from the Gulf Coast, (b) in partings from the Appalachian Province, and (c) in the roof-rock samples from the Eastern Interior and Gulf Coast Coal Provinces.
2. With the exception of the Gulf Coast roof-rock samples, zinc concentration is highest in Eastern Interior coal partings and roof rock.
3. Molybdenum content is higher in Eastern Interior partings and roof rock than in any of the other samples from the other provinces.
4. Lithium content is higher in Appalachian partings than in the other samples from other provinces.
5. With the exception of the Gulf Coast, chromium content appears to be generally the same in all samples from each province.
6. Antimony content is higher in all Eastern Interior samples than in samples from the other provinces.
7. Uranium content is highest in the Eastern Interior roof rock.

Enrichment of Accessory Elements in Coal

A convenient way of looking at the relative enrichment of accessory elements in coal is by comparing factors calculated by dividing an element's average crustal abundance (its Clarke value) into that element's concentration in the coal. Table 1.3 shows such factors for 30 accessory elements found in coal and coal-related rocks from the major and selected coal basins of the United States (Medlin 1977). Where no values are given for a particular element in the table, then that element is depleted in coals as compared to the earth's crust.

Only As, B, Ba, Sb, and Se are consistently enriched in all coals and coal-related rocks. As is the case for most means or "averages," the anomalous values tend to be masked. To circumvent this, a study of element minimum and maximum values and ranges is necessary. This allows identification of higher-than-average values. Examples of the deceiving nature of "averages" are the enrichment factors for cadmium and zinc in coal samples from the Interior Province. These two elements are not

TABLE 1.3 Elements Enriched in Coals and Coal-Related Rocks*

Element	Coal							Floor Rock		Partings		Roof Rock	
	Anth.	Appal.	Interior	G.C.	N. Great Plains	Rocky Mt.	Alaska	G.C.	E.I.	Appal.	E.I.	E.I.	G.C.
Ag	—	—	—	—	—	—	—	2.8	2.8	2.8	8.5	5.7	4.3
As	2.2	6.1	6.6	3.1	1.3	1.1	1.6	1.6	4.3	4.3	10.7	6.4	2.7
B	1	2	5	10	7	7	7	8	13	10	31	10	7
Ba	—	—	—	—	—	—	—	1.5	1.3	1.3	—	—	1.6
Be	—	—	—	—	—	—	—	1	2	1.5	4	1.5	1
Cd	—	1.5	—	1	—	—	1	1.6	1.3	—	5	2.7	1.4
Co	—	—	—	—	—	—	—	—	—	1.3	—	—	—
Cr	—	—	—	—	—	—	—	—	1	—	1	1.2	—
Cu	—	—	—	—	—	—	—	—	—	—	1.5	—	—
F	—	—	—	—	—	—	—	—	—	—	—	—	—
Ga	—	—	—	—	—	—	—	1.5	2	2.1	2.3	1.5	1.1
Ge	—	—	—	—	—	—	—	—	—	—	15	—	—
Hg	1.4	1.7	1.2	1.6	1	—	2.5	—	—	—	2.3	—	—
La	—	—	—	—	—	—	—	1.3	2.2	1.3	2	1.8	17
Li	1.2	—	—	—	—	—	—	2.5	4.5	6	4	2	2
Mn	—	—	—	—	—	—	—	—	—	—	—	—	—
Mo	1	1.3	1.3	—	1	1	1	—	—	—	14.6	8	—
Ni	—	—	—	—	—	—	—	—	—	—	2	—	—
Pb	—	—	1.5	—	—	—	—	—	3	2	3.6	1.5	—
Sb	3	4	4	3.5	2	1.5	9	4.5	5.5	4.5	7.5	5	4
Se	54	70	56	116	12	24	18	40	28	106	128	45	26
Sn	—	—	—	—	—	—	—	—	—	—	—	—	—
Sr	—	—	—	—	—	—	—	—	—	—	—	—	—
Th	—	—	—	—	—	—	—	—	1.5	1.6	1.2	1.5	1.1
U	—	—	—	—	—	—	—	1.3	1.6	1.6	1.7	3.2	1.3
V	—	—	—	—	—	—	—	1.1	1.1	—	—	1.1	1.1
Y	—	—	—	—	—	—	—	—	1.1	—	1.1	1	1.1
Yb	—	—	—	—	—	—	—	1	1.7	1.7	1.7	1.7	1.7
Zn	—	—	—	—	—	—	—	1.1	1.2	—	1.5	1.7	1.9
Zr	—	—	—	—	—	—	—	1.1	1.5	1	1.3	1	1.8

*Samples are from Anthracite (Anth.), Appalachian (Appal.), Interior, Eastern Interior (E.I.), and Gulf Coast (G.C.). Geometric mean concentration used in the calculation of enrichment values.

SOURCE: Swanson et al. (1976).

notably enriched in any of the coal or coal-related rocks as revealed by Table 1.3. However, close scrutiny of all data available to us shows that the ranges and minimum-maximum values for these elements in Interior Province coals (Table 1.3) are exceedingly variable.

It would appear that: (a) the widespread occurrence of coal having high zinc and cadmium values noted in the Interior Province is also true for the roof rock and coal partings from this province; (b) many of the chalcophile trace elements (Cd, Cu, Hg, and Zn, for example) and lithophile trace elements (Ba, Ca and Mg, for example) are more enriched in Eastern Interior coal partings than in the Appalachian and Gulf Coast samples; and (c) many of the chalcophile trace elements are more related to the high-sulfur coals than the low-sulfur western coals.

Examination of data for accessory elements in coal leads to the conclusion that relatively few accessory elements are actually concentrated in U.S. coals. Nevertheless, there are wide variations that require better geographic and stratigraphic delineation before they are fully understood. It is important to note that the concentration (enrichment) of an element in coal is not the only criterion for its study. Chemical reactivity, susceptibility to accumulation in wastes, and hazardous nature, etc., are equally important.

COAL-PREPARATION-PLANT WASTES

Coal-preparation plants are used largely to separate the carbonaceous material in raw coal from its associated high-ash refuse. This is primarily done by wet gravity-concentration methods, usually using water, though the flotation process, using heavy liquids such as oil, is also used to treat a modest tonnage. In recent years about 400 million tons of raw coal were treated annually in preparation plants producing 300 million tons of clean coal and approximately 100 million tons of refuse; little western coal is treated by coal-preparation techniques.

Better knowledge about the chemical and physical characteristics of the accessory elements in coal-cleaning wastes should be obtained: (1) to anticipate refuse disposal problems, such as ground- or surface-water pollution caused by these elements; and (2) to assist in the development of the technology for the economic recovery of as many of these elements as possible.

Sulfur

Prior to 1970, coal-preparation research was directed primarily at reducing ash content. Not until the introduction of the federal Clean Air Amendments of 1970 did it become clear that new studies were required to determine the efficiency with which sulfur could be removed from coal, the fate of sulfur and other accessory elements contained in the coal waste, and the environmental impact of the cleaning process itself (Warnke and Deurbrouck 1977). Since 1970, results of a number of studies have been published on gravity methods for the removal of pyritic sulfur from coal. For example, Helfinstine et al. (1971, 1974) found that only a small proportion of Illinois coals from 54 mines could be cleaned to produce a coal containing 1.5 percent or less sulfur. A more comprehensive report (Cavallero et al. 1976) presented results of a washability study of 455 coals from six coal-producing regions in the United States. Table 1.4 is a preliminary summary of theoretically possible effects of cleaning Northern Appalachian Region coal crushed to different size fractions. In contrast to the Illinois study, however, these data suggest a significant increase in the projected reserves of low-sulfur coal if all Appalachian coal were cleaned. Such differences in coal-cleaning potential are attributed to larger amounts of organic sulfur and finely divided pyrite in Illinois coals, both of which are little reduced by the conventional float/sink gravity methods employed.

Other Accessory Minerals and Elements

As a result of changes in mining practice and the general decline in availability of higher-quality coal beds, the ash content of raw coal has increased in the last few years. Recently, Bradley (1977) has shown that the ash-forming minerals in the fine discharge from conventional coal-preparation plants originate almost entirely from the shale associated with the coal being mined. Solubilities of most accessory elements in the wastes are controlled by these mineral phases in coal-cleaning wastes. The extent of concentration is dependent upon mineral composition, size distribution of discrete minerals within the whole

TABLE 1.4 Increase in the Low-Sulfur Coal Reserve Base of the Northern Appalachian Region as a Result of Cleaning Coal Crushed to Various Sizes (billion tons)

Product	<0.85 percent sulfur	0.85-3.00 percent sulfur	>3.0 percent sulfur
Raw coal	1.7	39.0	27.5
Crushed to pass 1½ in.			
Cleaned at 1.30	4.2	20.4	0.6
Cleaned at 1.60	4.2	43.4	14.2
Crushed to pass 3/8-in.			
Cleaned at 1.30	6.5	22.4	0.6
Cleaned at 1.60	6.2	44.6	9.9
Crushed to pass 14-mesh			
Cleaned at 1.30	7.1	21.7	0.4
Cleaned at 1.60	8.6	45.9	6.0

SOURCE: Modified from Warnke and Deurbrouck (1977).

coal, and the cleaning method employed. Examples of accessory elements and minerals in coal waste are shown in Table 1.5.

With the possible exception of sulfur, complete characterization of a sufficient number of coal-cleaning wastes has not been made to permit any kind of classification based on accessory element concentrations, coal province or type of cleaning practice used. Nevertheless, some studies have been conducted to determine their composition. One of the more complete studies (Bland et al. 1976) gave data for bulk composition (ash, Btu content, etc.), major elements, and normative mineralogy. Trace elements in preparation wastes from various coals are given in Table 1.6 (Robl et al. 1976).

Trace elements associated with the organic phases of coal are removed during coal cleaning to a much lesser extent than those in the mineral matter. Accessory elements in coal that may be in organic combination are shown in Table 1.7 (Gluskoter et al. 1977). In addition, for many coals, a significant portion of the sulfur is organically combined. At present, little can be done to prevent the entry of those elements with a high organic affinity into the cleaned coal. Unless methods for their removal are developed, they will become a particular problem in power generation and coke production, as well as in gasification and liquefaction processes.

Preliminary estimates of the amount of organically associated elements have been calculated from washability curves on which corrections for the amount of inseparable mineral matter in the lightest (cleanest) coal fraction had been made (Gluskoter et al. 1977). These amounts were compared with those determined independently in "mineral-free" (low-ash) organic residues from acid-extracted coals (Kuhn et al. 1978). Typical comparisons of accessory element amounts in whole coal and in the residual organic phase of three coals are given in Table 1.8.

TABLE 1.5 Accessory-Element/Coal-Mineral Associations

Mineral Group, Principal Elements	Element With Positive* Correlation With Mineral
Sphalerite, ZnS	Zn, Cd, (Hg, B)
Galena, PbS	Pb (Hg)
Apatite, $Ca_5(PO_4)_3(F,CO_3)$	Ca, P, F
Pyrite, FeS_2	Ni, Cu (As, Be, Sb)
Kaolinite, aluminosilicate	Si, Al, Ti, K, (B, Cu, F, Hg, Sn, V)
Quartz, SiO_2	(B, Cr, Mn, Cd, Mo, Se, V, Zn)
Calcite, $CaCO_3$	Mn (B, Cd, Mo, Se, V)

*Elements in parentheses in this column have not been detected in specific mineral phases; however, a positive correlation existed.

SOURCE: Ruch et al. (1974).

TABLE 1.6 Minor and Trace Element Content for Refuse Associated with Individual Coal Seams

	Number of Samples	Ba	Co	Cu	Ni	Rb	Sr	Y	Zn	Zr
					(Parts Per Million)					
EASTERN COAL FIELD										
All Eastern (Present)	37	749 (441-1227)*	29 (5-69)	59 (13-113)	55 (23-96)	180 (58-225)	259 (141-1108)	42 (23-75)	114 (34-393)	253 (166-446)
All Eastern (Past)	9	739 (610-1043)	20 (7-34)	45 (13-63)	46 (18-64)	160 (74-201)	205 (99-369)	33 (15-46)	96 (38-155)	249 (137-414)
Elkhorn No. 3	10	704 (578-792)	43 (27-69)	62 (44-97)	55 (40-86)	167 (154-186)	234 (176-387)	30 (23-36)	121 (100-168)	201 (166-239)
Lower Elkhorn	11	754 (669-892)	21 (13-27)	51 (44-57)	51 (46-60)	193 (173-213)	212 (177-246)	32 (27-39)	93 (70-108)	230 (212-243)
Hazard No. 4	3	480 (459-509)	8 (5-9)	28 (13-45)	30 (23-36)	85 (58-119)	214 (151-271)	49 (33-78)	58 (34-79)	481 (404-594)
Hazard No. 5A	1	657	32	61	63	167	214	38	117	205
WESTERN COAL FIELD										
All Western (Present)	11	686 (305-1883)	76 (45-113)	95 (60-138)	98 (72-137)	141 (62-341)	198 (91-354)	36 (0-57)	309 (88-1274)	179 (111-251)
All Western (Past)	4	1194 (544-2343)	50 (28-101)	43 (18-100)	43 (23-87)	153 (130-175)	164 (149-197)	25 (16-43)	72 (38-151)	167 (182-172)
No. 9	6	1144 (561-1183)	79 (68-87)	94 (81-103)	109 (87-137)	202 (122-341)	111 (91-145)	18 (0-30)	275 (88-526)	138 (111-164)
No. 11	6	383 (338-541)	86 (75-100)	75 (66-89)	89 (73-94)	116 (103-130)	131 (102-182)	30 (21-36)	237 (113-372)	161 (148-183)

*Numbers in parentheses indicate range in values.

SOURCE: Robl et al. (1976).

TABLE 1.7 Association of Accessory Elements with Coal or Ash Constituents for Four Illinois Coals*

Organic Affinity	Intermediate Organic Affinity		Inorganic Affinity	
Ge	Co	Cr	Al	Mn
Be	Ni	Cu	Si	Fe
B	Ti	K	Zr	As
Sb	Ga	Mg	Ca	Cd
V	Se	Hg	Pb	Zn

*It must be cautioned that these affinities are general in nature, and substantial quantities of those elements with a high organic affinity may be found in the refuse and, conversely, elements with a high inorganic affinity may be found in the coal.

SOURCE: Gluskoter et al. (1977).

These and similar data for other elements and coals suggest that the total amount of the accessory elements in the organic phase, such as Al, Ca, Fe, Si, Mn, and As, is relatively low (about 200 parts per million or less); sulfur is excluded. Therefore, the major amounts of these elements are most likely contained in the coal mineral matter, significant amounts of which can be removed.

There are methods being evaluated that could improve the efficiency with which both organic and inorganic accessory elements are removed from coal. One is coal-maceral separation in the preparation plant by gravity separation or by froth flotation (Aplan 1976). Dull constituents such as durain and fusain commonly contain more mineral matter (accessory elements) than do the bright constituents. Dull constituents also have a higher specific gravity and respond less readily to the flotation process than do the bright macerals. Thus, new multiple-stream coal-processing plants currently being tested may partition accessory elements in a different manner (McConnell and Statler 1976).

New Coal-Cleaning Techniques

Warnke and Deurbrouck (1977) described a number of new or modified coal-preparation techniques that are being tested by the U.S. Bureau of Mines. These include reagent-starved froth flotation, magnetic separation, and two-stage flotation. Assessment is also under way for the combined use of physical coal cleaning and less-than-full-scale stack-gas scrubbing. The effects of these processes on the removal, disposal, and redistribution of accessory elements are still being evaluated, but it is likely that some of the resulting wastes will have chemical and physical properties that differ from those of present-day coal-cleaning wastes.

In addition to physical cleaning methods, the dissolution of ash-forming mineral contaminants from coal has also been accomplished using acids, alkalies, and oxidation-reduction reagents. The contaminants are then removed as a waste product by leaching either with water or other suitable solvents. These approaches have been reviewed by Mezey et al. (1976a, b) and include the alkali hydrothermal treatment, for reducing the sulfur content of high-sulfur coals, developed by the U.S. Bureau of Mines and Battelle Memorial Institute. The extent of removal of pyritic sulfur after treatment with alkali under conditions of the Battelle hydrothermal coal process (BHCP) ranged from 87 to 99 percent. The effect on removal of some trace elements is given in Table 1.9. High-

TABLE 1.8 Comparison of Element Concentrations from Extrapolations of Coal-Washability Curves with Values Determined in Mineral-Free Coal

Element	Raw Coal	Extrapolation*	"Mineral-Free" Coal**
		Western Coal	
Al	1.40 %	0.0 %	87 ppm
Si	1.40 %	0.0 %	87 ppm
Na	.17 %	.15 %	1.4 ppm
B	37 ppm	37 ppm	5.3 ppm
Cu	4.7 ppm	2.0 ppm	<3 ppm
Ni	2.6 ppm	1.14 ppm	1.5 ppm
		Pocahontas #4	
Mg	.06 %	.00 %	18 ppm
Org S	.50 %	.60 %	.47 %
Be	.88 ppm	.94 ppm	.11 ppm
Se	5.8 ppm	1.1 ppm	1.0 ppm
Ba	180 ppm	118 ppm	33 ppm
Cs	2.0 ppm	.0 ppm	.2 ppm
Br	24 ppm	27 ppm	16 ppm
Mn	14 ppm	1.6 ppm	.5 ppm
		Illinois #6	
Fe	1.83 %	0.0 %	55 ppm
K	.17 %	0.0 %	1.3 ppm
V	32 ppm	9.2 ppm	8.5 ppm
Co	7.7 ppm	.12 ppm	.2 ppm
Zn	2668 ppm	0.0 %	3 ppm
As	31 ppm	.0 ppm	.21 ppm

*Values from adjusted washability curves

**Values from acid extracted coal

SOURCE: Kuhn et al. (1978).

TABLE 1.9 Extraction of Trace Elements by the Alkaline Desulfurization Process (BHCP*)

Metal	Concentration, ppm**	
	Raw Coal	Leached Product
Lithium	15	3
Beryllium	10	3
Boron	75	4
Phosphorus	400	80
Potassium	5000	200
Vanadium	40	2
Arsenic	25	2
Molybdenum	20	5
Barium	25	4
Lead	20	5
Thorium	3	0.5

*Battelle hydrothermal coal process.
**Average values for 3 Ohio coals: CN719-Seam 6, HN658-Seam 6A, and Jackson-Seam 4.

SOURCE: Mezey et al. (1976b).

sulfur coals treated hydrothermally with alkali and then by an acid at the Bureau of Mines showed significant removal of ash (62 to 95 percent) and pyritic sulfur.

Results of pyrite removal by the Meyers process have been compared to removal attainable by float-sink separation at a specific gravity of 1.9 (Hamersma et al. 1974). Pyrite removal ranged from 83 to 99 percent for the Meyers process, and sulfur values were consistently lower than those attainable by conventional float-sink methods. The ferric sulfate treatment also reduced the As, Be, Cr, Li, Mn, Ni, Pb, Se, and Zn contents of coals. The amounts of As, Mn, and Zn were significantly lowered in all the coals studied; B, Cu, and F showed insignificant levels of removal.

Byproduct Recovery

Accessory element recovery from coal-processing wastes is a possibility with ample precedents in coal and other mining activities (Mining Engineering 1955, Modern Metals 1960, Sun and Savage 1969, and Brock 1957). A recent laboratory study (Ford et al. 1976) has shown that during fine-coal cleaning with the shaking table the refuse zones are enriched in As, Cd, Cr, Cu, F, Pb, Mn, Hg, Ni, Se, V, and Zn (Table 1.10). Recoveries of about 30 percent were achieved. While far from being of commercial-product grade, these preconcentrates may provide feed for a subsequent upgrading process. Estimates made from the published reports of Deurbrouck and Jacobsen (1974), and Schultz et al. (1975) indicate that the coal refuse will generally contain more than 2.5 times the trace-element content of raw coal. Similarly, for Illinois coals, more than 50 percent of the following trace elements were contained in the 20 percent of the raw coal (refuse fraction) removed by float-sink methods (Miller 1974): Al, As, Ca, Cd, Co, Cr, Cu, Fe, Ga, Hg, K, Mn, Mo, Ni, Pb, Sb, Se, Si, Ti, Zn, and Zr.

In a laboratory study of the washability of 10 samples of -14 mesh coal, Cavallero et al. (1978) have shown that the ratio of the trace-element amount in the 1.60 sink fraction as compared to the amount of that element in the float fraction is generally 3 to 10 for Cd, Cr, Cu, F, Hg, Ni, and Pb in some eastern coals; much higher ratios were delineated for Mn. The ratio in a western sample is much less. The above study and that of Ford et al. (1976) clearly indicate the

TABLE 1.10 Trace Elements Removed by Use of the Shaking Table for Coal Cleaning

Element	Element Content of Shaking Table Refuse Zones (Range for 8 samples in ppm unless otherwise stated)	% of Trace Element Removed
As	13 - 969	41
Be	0.5 - 5.1	6
Cd*	2.1 - 4.6	21
Cr	17 - 98	17
Cu	15 - 109	23
F	23 - 281	8
Hg (ppb)	232 - 6930	30
Pb	31 - 821	32
Mn	48 - 1180	37
Ni	37 - 121	22
Se	5 - 67	28
V	7 - 157	13
Zn	66 - 1157	33
Ash (%)	58 - 83	33
Pyritic sulfur	2.7 - 39	32
Weight loss to refuse		12

* One sample only.

SOURCE: Ford et al. (1976).

potential of gravity separation to achieve a concentration of several of these trace elements.

Capes et al. (1974) have shown that the tailings from the spherical agglomeration process are substantially enriched in As, Ba, Cr, Cu, Pb, Mn, Mo, Ni, Sb, V, and Zn. Froth flotation may be expected to show a similar response.

Accessory element recovery from coal-preparation-plant refuse is economically attractive because the production of the coal has borne the mining and preparation costs. A logical feed stream for such a recovery process would be the refuse product from the fine-cleaning sections. Major additional crushing would be avoided. A preconcentrate produced by traditional gravity-concentration techniques could furnish the feed to a small plant using gravity-concentration, flotation, hydrometallurgy, or other separation techniques to produce a final product. This recovery system would probably be most efficient if attached to a large preparation plant employing extensive fine-cleaning circuits, or at a centralized recovery plant which would receive preconcentrates from several satellite preparation plants. Careful selection of those coal beds which show high concentrations of selected elements in those minerals that may be readily concentrated (for example, zinc recovery from sphalerite in some Illinois and Iowa Interior Province coals) would help ensure success.

Alternatively, natural or induced leaching, by sulfuric acid, may allow for recovery of heavy-metal ions from the leachate by hydrometallurgical techniques, such as precipitation, adsorption, ion exchange and solvent extraction. The processes used in leaching of copper refuse may serve as a guide.

COAL-FIRED POWER-PLANT WASTES AND EMISSIONS

Composition of Ash

The amount of waste material generated by coal-fired power plants in combustion and stack-gas cleaning poses an environmental concern. The incorporation of noncombustible shale material into the coal results in an ash that is similar in major element content to ignited shale. A variable increase in iron content due to pyrite in the coal commonly occurs in the ash, and an increase in calcium in the ash can arise from carbonate minerals in the coal or from limestone used in stack-gas scrubbers. Coal ash usually contains some unburned carbonaceous material.

The chemical and mineral compositions of laboratory ash, bottom ash and fly ash have been reported in many publications (for example, Rees 1964; Abernethy 1969; Ruch et al. 1974; Linton et al. 1976; Fischer 1976; Mitchell and Gluskoter 1976; Bolton et al. 1973; Stephens 1974; and Ray and Parker 1977). The accessory element composition of coal ashes can vary considerably depending on the source of coal and the combustion process employed. Fly ash makes up from 10 to 85 percent of coal-ash residue (in most modern plants it is 70 to 80 percent) and usually occurs as spherical particles (.5 to 100 microns) called cenospheres. Bottom ash is composed of coarser and heavier particles than fly ash and contains a high amount of a glassy component called slag. Differences in the concentrations of various elements in fly ash and bottom ash are shown in Table 1.11 (Ray and Parker 1977).

Stack-Gas Scrubber and Fluidized-Bed Combustion Wastes

Lime, limestone, and double-alkali scrubbing processes to remove sulfur oxides from power-plant stack gases (flue-gas desulfurization [FGD]) have undergone extensive testing, and some plants, new and retrofitted, are already in operation. It is recognized that FGD produces large quantities of sludge consisting primarily of water and calcium-magnesium sulfates and sulfites. The sheer magnitude of nonregenerable wastes from lime and limestone FGD presents a potentially serious disposal problem. It is estimated for a 500-megawatt power plant burning 3.5 percent sulfur coal that the volume of solids (50 percent moisture) produced annually would occupy about 6,000 acre-feet (Elder 1974). Studies of the composition, solubility and disposal of FGD sludges have been made by Rosshoff et al. (1977). Table 1.12, from their publication, gives a range of concentrations of chemical constituents in FGD sludges. They found that there is a direct relationship between trace-element amounts in the sludge and those in the coal. Further, a direct relationship between trace-elements in sludge and fly ash suggested that fly ash is the principal component containing the trace elements in the sludge. Rosshoff et al. also found that the most persistent pollution potential came from percolation of wastes through the sludge and into the subsoil.

Another solid waste, consisting mainly of lime and calcium sulfate, is produced from fluidized-bed combustion (FBC) of coal. Although the solid wastes from this process when using limestone (or dolomite) as the fluidizing medium may be regenerable to a degree, they must eventually be discarded in an environmentally acceptable manner. The primary difference between the FGD and the FBC solid wastes is the water content; fluidized-bed wastes are dry whereas flue-gas desulfurization wastes are disposed of as a wet sludge. Also, FBC waste includes all of the coal ash, whereas scrubber sludge includes only part of the fly ash. Table 1.13 includes examples of analyses of two wastes resulting from fluidized-bed combustion (Battelle Columbus Laboratories 1977). Of all the advanced direct-combustion processes considered by the National Research Council (1977a), the most promising for first-stage development was atmospheric-pressure FBC. It is claimed to have a high potential for controlling gaseous emissions more economically than existing methods.

Scrubbing processes are being developed using absorbers capable of being at least partly regenerated. These include sorbents such as magnesia, ammonia, citrate (U.S. EPA 1974b), and a ferrous-sulfate/iron-oxide mixture (McGauley and Dor 1975). If developed on a commercial scale, these processes would help alleviate the potential solid-waste disposal problems associated with stack-gas scrubbing.

TABLE 1.11 Comparison of Fly Ash and Bottom Ash from Various Utility Plants

Compound or Element	Plant 1		Plant 2		Plant 3		Plant 4		Plant 5		Plant 6	
	FA	BA	FA	BA	FA	BA	FA	BA	FA	BA	FA	BA
SiO_2,%	59.	58.	57.	59.	43.	50.	54.	59.	NR	NR	42.	49.
Al_2O_3,%	27.	25.	20.	18.5	21.	17.	28.	24.	NR	NR	17.	19.
Fe_2O_3,%	3.8	4.0	5.8	9.0	5.6	5.5	3.4	3.3	20.4	30.4	17.3	16.0
CaO,%	3.8	4.3	5.7	4.8	17.0	13.0	3.7	3.5	3.2	4.9	3.5	6.4
SO_3,%	0.4	0.3	0.8	0.3	1.7	0.5	0.4	0.1	NR	0.4	NR	NR
MgO,%	0.96	0.88	1.15	0.92	2.23	1.61	1.29	1.17	NR	NR	1.76	2.06
Na_2O,%	1.88	1.77	1.61	1.01	1.44	0.64	0.38	0.43	NR	NR	1.36	0.67
K_2O,%	0.9	0.8	1.1	1.0	0.4	0.5	1.5	1.5	NR	NR	2.4	1.9
P_2O_5,%	0.13	0.06	0.04	0.05	0.70	0.30	1.00	0.75	NR	NR	NR	NR
TiO_2,%	0.43	0.62	1.17	0.67	1.17	0.50	0.83	0.50	NR	NR	1.00	0.68
As,ppm	12.	1.	8.	1.	15.	3.	6.	2.	8.4	5.8	110.	18.
Be,ppm	4.3	3.	7.	7.	3.	2.	7.	5.	8.0	7.3	NR	NR
Cd,ppm	0.5	0.5	0.5	0.5	0.5	0.5	1.0	1.0	6.44	1.08	8.0	1.1
Cr,ppm	20.	15.	50.	30.	150.	70.	30.	30.	206.	124.	300.	152.
Cu,ppm	54.	37.	128.	48.	69.	33.	75.	40.	68.	48.	140.	20.
Hg,ppm	0.07	0.01	0.01	0.01	0.03	0.01	0.08	0.01	20.0	0.51	0.05	0.028
Mn,ppm	267.	366.	150.	700.	150.	150.	100.	100.	249.	229.	298.	295.
Ni,ppm	10.	10.	50.	22.	70.	15.	20.	10.	134.	62.	207.	85.
Pb,ppm	70.	27.	30.	30.	30.	20.	70.	30.	32.	8.1	80.	6.2
Se,ppm	6.9	0.2	7.9	0.7	18.0	1.0	12.0	1.0	26.5	5.6	25.	0.08
V,ppm	90.	70.	150.	85.	150.	70.	100.	70.	341.	353.	440.	260.
Zn,ppm	63.	24.	50.	30.	71.	27.	103.	45.	352.	150.	740.	100.
B,ppm	266.	143.	200.	125.	300.	70.	700.	300.	NR	NR	NR	NR
Co,ppm	7.	7.	20.	12.	15.	7.	15.	7.	6.0	3.6	39.	20.8
F,ppm	140.	50.	100.	50.	610.	100.	250.	85.	624.	10.6	NR	NR

SOURCE: Ray and Parker (1977).

TABLE 1.12 Range of Concentrations of Chemical Constituents in Flue-Gas Desulfurization Sludges

Scrubber Constituent	Sludge Concentration Range: Liquor, mg/l (except pH)[a]	Sludge Concentration Range: Solid, ppm[b]
Aluminum	0.03 - 2.0	—
Arsenic	<0.004 - 1.8	0.6 - 52
Beryllium	<0.002 - 0.18	0.05 - 6
Cadmium	0.004 - 0.11	0.08 - 4
Calcium	180 - 2,600	105,000 - 268,000
Chromium	0.015 - 0.5	10 - 250
Copper	<0.002 - 0.56	8 - 76
Lead	0.01 - 0.52	0.23 - 21
Magnesium	4.0 - 2,750	—
Mercury	0.0004 - 0.07	0.001 - 5
Potassium	5.9 - 100	—
Selenium	<0.0006 - 2.7	2 - 17
Sodium	10.0 - 29,000	(4.8)
Zinc	0.01 - 0.59	45 - 430
Chloride	420 - 33,000	(0.9)
Fluoride	0.6 - 58	—
Sulfate	600 - 35,000	35,000 - 473,000
Sulfite	0.9 - 3,500	1,600 - 302,000
Chemical Oxygen Demand	<1 - 390	—
Total Dissolved Solids	2,800 - 92,500	—
pH	4.3 - 12.7	—

[a] Liquor analyses were conducted on 13 samples from 7 power plants burning eastern or western coal and using lime, limestone, or double-alkali absorbents.

[b] Solids analyses were conducted on 6 samples from 6 power plants burning eastern or western coal and using lime, limestone, or double alkali.

SOURCE: Rosshoff et al. (1977).

Coal-Fired Power-Plant Emissions

Many investigators have studied the probable partitioning of elements during coal combustion and the expected amount of stack emissions, gas and particulate, at several power plants. Kaakinen et al. (1975) found in a study of inlet and outlet streams in a Colorado power plant that of 12 elements, all could be accounted for in terms of mass balance except selenium (for which 60 percent of the mass was unaccountable) and mercury (for which nearly 100 percent was unaccountable); the selenium and mercury presumably volatilized and escaped through the stack.

TABLE 1.13 Examples of Typical Coal and Sorbent Input and Output Compositions (major constituents) for FBC Combustors (weight percent)

Compound	Coal, Pittsburgh #8[1]	Limestone, #1359-Grove[2]	Dolomite, #1337-Pfizer[1]	Coal Ash[1]	Atmospheric FBC Waste[3]		Pressurized FBC Waste[3]	
					Limestone, #1359	Dolomite, #1337	Limestone, #1359	Dolomite, #1337
$CaSO_4$	—	—	—	—	43.7	31.5	60.6	64.1
CaO	—	3.8	28.9	1.9	54.0	30.2	37.4	6.6
$CaCO_3$	—	92.3	—	—	—	—	—	—
MgO	—	0.3	22.9	0.6	(a)	36.7	(a)	22.9
Fe_2O_3	—	0.1	0.2	27.3	(a)	(a)	(a)	(a)
SiO_2	—	0.5	0.5	45.3	(a)	(a)	(a)	(a)
Al_2O_3	—	—	—	21.2	(a)	(a)	(a)	(a)
C	71.2	—	—	—	—	—	—	—
S	4.3	—	—	—	(b)	(b)	(b)	(b)
H_2	5.1	—	—	—	—	—	—	—
O_2	6.3	—	—	—	—	—	—	—
N_2	1.3	—	—	—	—	—	—	—
H_2O	3.3	—	47.4[c]	—	—	—	—	—
Ash	8.5	—	—	—	—	—	—	—
Other Trace Elements & Compounds	—	—	—	—	2.3	1.6	2.0	1.2

SOURCE:
(1) Battelle/Columbus Laboratories, open literature.
(2) Exxon Research and Engineering.
(3) Westinghouse Research Laboratories.

(a) Included in other.
(b) Included in $CaSO_4$ value.
(c) $H_2O + CO_2$

Turner and Strojan (1976) gave estimates of the annual atmospheric discharges from 3 power plants for 14 trace elements (Table 1.14) and U.S. EPA (1975a) listed 18 trace elements as being enriched in fly ash in the flue gas of 3 power plants they studied. Klein et al. (1975) partitioned 38 elements among bottom ash, fly ash, and discharge to the atmosphere (Table 1.15). In addition to the elements (or compounds) mentioned above, Turner and Strojan (1976) and U.S. EPA (1975a) also cite Ba, Co, Cr, Mn, Sc, Sr, V, Fe, Ni, and Ag. Thus, a survey of the literature implicates at least two dozen elements as known or suspected emittents from coal-fired power plants. Moreover, polycyclic organic compounds have also been identified in fly ash from coal-fired power plants (Natusch 1976).

TABLE 1.14 Estimated Annual Atmospheric Discharge from Coal-Burning Power Plants

Element	Savannah River Power Plant (83 MW)	Allen Steam Plant (870 MW)	Mohave Generating Station (1580 MW)	Hypothetical Station (1400 MW)
		Kilograms		
As	4,330	105	136	1,198
Ba	5,243	158	7,700	284
Cd		11	<9	120
Co	948	11	27	120
Cr	2,265	158	145	73
Hg		53	109	233
Mn	4,396	105	200	11,984
Pb		105	327	2,365
Sb	235	105	27	237
Sc	526	5	27	237
Se		210	927	237
Sr	14,987		1,782	
V	3,265	210	291	2,365
Zn		1,051	400	11,984

Note: Missing values indicate no available estimates.

SOURCE Turner and Strojan (1976).

TABLE 1.15 Partition of Elements in Coal Combustion Residues

Group I

Elements Concentrated Approximately Equally in Bottom Ash and Flyash

Al	Ce	Fe	La	Rb	Sm	Th
Ba	Co	Hf	Mg	Sc	Sr	Ti
Ca	Eu	K	Mn	Si	Ta	

Group II

Elements Preferentially Concentrated in the Flyash

As	Ga	Sb
Cd	Mo	S
Cu	Pb	Zn

Group III

Elements Tending to be Discharged to Atmosphere as Vapors

Hg		Cl
		Br

Note: Cr, Cs, Na, Ni, U, and V were judged intermediate between Groups I and II.

SOURCE: Klein et al. (1975).

Environmental Effects of Emissions

Theoretically, all naturally occurring elements in coal (and many compounds produced by combustion) will exist in the stack gas in at least some concentration level, however small. What is more important in an environmental context is not whether an element can be measured in the emissions, but whether or not its effects can be observed in the local environment.

Connor et al. (1976a, b) and Gough and Erdman (1976) found exponentially decreasing amounts of selenium in lichen, grass, and sagebrush with increasing distance from two western power plants (Figure 1.1). Several such elemental trends were judged to be statistically significant in lichen and sagebrush downwind from the power plant in Wyoming (Table 1.16). Similar trends in soil associated with this vegetation were not detected, which supports previous generally negative findings based on analyses of soil near power plants (Turner and Strojan 1976). A comparison of element amounts in lichen, two species of sagebrush, soil dust, and fly ash near the Wyoming power plant suggested that some of the elements enriched in vegetation probably reflect simple scavenging of windborne soil or fly ash derived from the power-plant site itself (a site of heavy traffic and an exposed pile of fly ash).

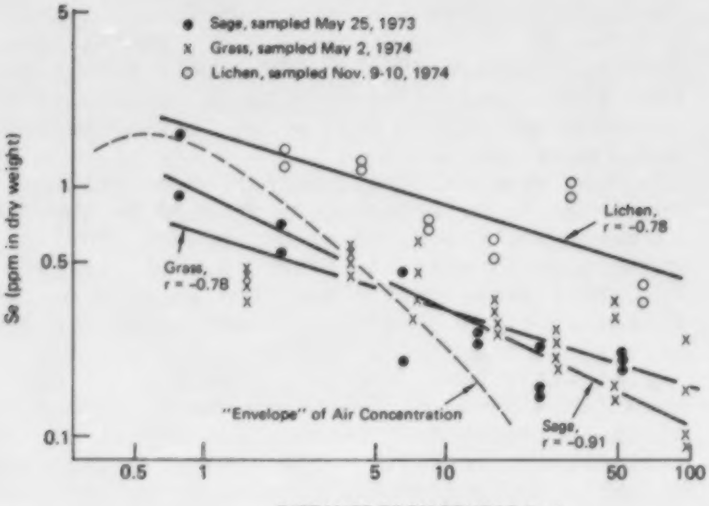


FIGURE 1.1 Selenium in lichen (*P. chlorochroa*), grass (*O. hymenoides*), and sagebrush (*A. tridentata*) near coal-fired power plants in Wyoming (lichen and sagebrush) and New Mexico (grass). Correlation coefficients (r) are statistically significant at the 0.05 probability level.

SOURCE: Adapted from Connor et al. (1976a, b) and Gough and Erdman (1976).

TABLE 1.16 Elements in Sagebrush and Lichen Showing Decreasing Trends Going Away from Power Plants

Element	Sage		Lichen
	A. tridentata	*A. cana*	*P. chlorochroa*
Li	+	++	++
U	+	++	++
V	++	++	+
Cr	+	++	+
F	?	++	++
S	++	++	nd
Co	+	+	nd
Se	++	—	++
Sr	++	—	++
Ni	++	—	+
Pb	—	++	—
Zn	++	—	—
As	—	+	—
Cu	+	—	—

Elemental trends away from Wyoming powerplant
++ strong, significant — not significant
+ weak but significant nd not determined

SOURCE: Conner et al. (1975b), Gough and Erdman (1976), and unpublished data.

The amounts of some elements, however, cannot be so explained (S, Se, Cu, Pb, Zn, Sr, and perhaps V, F, and Ni) and these must be regarded as possible stack-gas emittents. This work further suggested that, for the most part, measurable impacts of trace-elements on native vegetation around power plants will rarely extend beyond 10 kilometers from the plant site (Figure 1.1).

Most trace elements appear to be emitted in or on fly-ash particles too small to be effectively trapped in the stack using conventional scrubber and precipitator equipment. Natusch et al. (1974) found the highest concentrations of Pb, Ti, Sb, Cd, Se, As, Ni, Cr, Zn, and S in the finer sizes of fly ash from eight U.S. power plants. Recent studies by Fisher et al. (1977) have confirmed the results of Natusch et al. showing that apparent density and concentrations of trace elements (Table 1.17) vary inversely with fly-ash particle size. This relationship was not entirely due to elemental volatility because some of the normally refractory elements--U, Cr, Fe, Mn, Ba, and Sr--are included (Table 1.17). The inverse particle-size dependency for these elements was attributed to mineral decomposition of, for example, the carbonates, and elemental-organic combinations. Further, there is a tendency for many elements to be concentrated on the surface of the fly-ash particle presumably as condensates during the temperature drop from combustion to emission (Linton et al. 1976).

Some elements are emitted largely in the gaseous state, particularly the oxides of S, N, and C. Also included here, perhaps, are HF and elemental Se, Hg, Sb, As, Cd, and Mo (Vaughan et al. 1975). Much attention has focused on the potential for "acid rain" resulting from hydrolysis of sulfur dioxide in the atmosphere. Table 1.18 lists the chronic low-level effects of various pollutants on plants (Auerbach 1975 cited in Carrier 1977). Gordon and Tourangeau (1975) and Gordon et al. (1976, 1977) discussed the kinds of vegetation damage attributed to sulfur dioxide and hydrofluoric acid pollution in the northern Great Plains. In one study, fluoride concentrations in pine needles were indirectly related to percentage of healthy needles (Table 1.19). In another, needle retention on pine was substantially reduced in polluted areas. In still another, 4 hours of exposure to 1 to 2 parts per million of sulfur dioxide resulted in slight to severe foliar injury. Thus, even for combustion of low-sulfur western coals, it may be necessary to reduce sulfur (and fluorine) emissions to prevent damage to the more susceptible plant species.

Control of Emissions

Among the most recent studies on the control of particulate and gaseous emissions from coal-fired power plants are those being conducted by the Electric Power Research Institute (EPRI) on fabric filtration of fly ash (EPRI 1976, Carr et al. 1977, and Carr and Teixeira 1977). They report very high retention efficiencies for submicron particles ranging from 99.4 to 99.9 percent for fabric filters used in a small (12 megawatt) coal-fired stoker boiler. Indeed, collection efficiency in the baghouse was virtually independent of particle size. This is not necessarily true of other collectors such as electrostatic precipitators. Contrary to previous reports, trace-element enrichment appeared to reach a

TABLE 1.17 Elemental Concentrations Dependent[1] on Particle Size (parts per million except otherwise indicated)

Element	Technique	Fraction 1 (VMD = 20 μm)	Fraction 2 (VMD = 6.3 μm)	Fraction 3 (VMD = 3.2 μm)	Fraction 4 (VMD = 2.2 μm)	Enhancement Factor[2]
Cd	AAS[3]	0.4(0.2)	1.6(0.3)	2.8(0.4)	4.6(0.2)	11.5
Zn	AAS	68(1)	189(4)	301(10)	746(218)	11.
Se	INAA[4]	19(2)	59(2)	78(2)	198(20)	10.4
As	INAA	13.7(1.3)	56(14)	87(9)	132(22)	9.6
Sb	INAA	2.6(0.1)	8.3(0.4)	13.0(0.7)	20.6(0.7)	7.9
W	INAA	3.4(0.2)	8.6(1.6)	16(2)	24(2)	7.1
Mo	INAA	9.1(2.5)	28(1.4)	40(5)	50(9)	5.5
Ga	INAA	43(12)	116(52)	140(23)	178(90)	4.1
Pb	AAS	73(3)	169(2)	226(4)	278(3)	3.8
V	INAA	86(44)	178(17)	244(18)	327(40)	3.8
U	INAA	8.8(1.9)	16(3)	22(4)	29(4)	3.3
Cr	AAS	28(3)	54(3)	66(3)	71(4)	2.5
Ba(%)	AAS	0.168(0.001)	0.245(0.002)	0.320(0.013)	0.409(0.018)	2.4
Cu	AAS	56(1)	89(1)	107(4)	137.(1)	2.4
Be	AAS	6.3(0.2)	8.5(0.2)	9.5(0.3)	10.3(0.5)	1.6
Mn	AAS	209(7)	231(5)	273(7)	309(3)	1.5
Si(%)	AAS	29.6(0.7)	28.0(0.1)	27.5(0.3)	26.8(0.1)	0.90

[1] Concentration dependence with particle size was determined qualitatively with the criterion that consistent concentration trends beyond experimental uncertainty were observed for each fraction.

[2] Ratio of concentration in Fraction 4 to that in Fraction 1.

[3] AAS values are the averages of two independent determinations; the ranges are given in parentheses.

[4] INAA values are the weighted averages of three independent determinations; uncertainties (in parentheses) are the largest of twice the weighted standard deviation, the range, or an estimate of the accuracy.

VMD = Volume Mean Diameter

SOURCE: Fisher et al. (1977).

TABLE 1.18 Types of Chronic, Low-level Effects on Plants and Probable Mechanisms Involved

Type of Effect	Probable Mechanisms	Pollutants Involved[a]
Reduced growth	Decreased photosynthesis	SO_2, O_3, NO_x, HF, PAN,* Pb
	Increased respiration	HF, SO_2
	Biochemical changes	
	Enzyme inhibition	SO_2, O_3, PAN, HF, As
	Electron (energy) transport	HF, O_3, PAN
	Effects on photopigments	SO_2, HF, O_3, PAN, NO_x
	Stomatal function	SO_2, O_3
	Membrane permeability	O_3, PAN, SO_2, HF, metals
	Premature senescence of leaves	SO_2, O_3, PAN, NO_2
	Physical changes	
	UV reflectivity	Acid rain
	Heat exchange	Acid rain
	Gas exchange	Acid rain
	Changes in symbiosis	O_3, acid rain
	Effects on nutrient flux	SO_2, acid rain
Reduced reproduction	Reduced carbohydrate availability for reproductive processes	SO_2, O_3, HF, PAN, Pb, NO_2
	Effects on reproductive processes	
	Flower or fruit production	Smog, HF, SO_2
	Pollen germination or tube elongation	SO_2, O_3, HF
	Mutagenesis	SO_2
	Effects on pollinating insects	HF
Increased morbidity	Inadequate carbohydrate supply to support autotrophic respiration and resist diseases; reduced growth and loss of ability to compete with other vegetation	SO_2, O_3, HF, PAN, NO_2, heavy metals

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[a] Includes pollutants for which specific effects have been documented and those whose biochemical symptomology strongly implicate them as probable causal agents.

*PAN = peroxyacetylnitrate, a reactive class of compounds in photochemical smog that causes eye irritation.

SOURCE: Auerbach (as given in Carrier 1977).

maximum for particles in the .3 to 10 millimicron diameter size range. Collection efficiency for specific elements, such as Al, Si, Ti, Fe, Zn, Pb, Ni, and Cu, was in no case worse than 99 percent and frequently was better.

From these findings, it appears that power-plant emissions for many of the trace elements can be controlled with very high efficiency in a baghouse. This represents a major finding, since it has been assumed that an entirely new technology might be required for their control. Furthermore, it now appears likely that by a combination of baghouse temperature control and stack-gas scrubbing, volatile trace-element emissions (for example, arsenic, selenium, and mercury) and polycyclic organic emissions (POM) (such as benzo(a)pyrene) can be controlled through existing technology. Research on this subject is clearly needed, but preliminary considerations indicate that selenium, arsenic, and polycyclic organic emissions can be condensed by lowering the baghouse temperature to about 200°F, while stack-gas scrubbers (130 to 135°F) can condense or chemically react with a significant portion of the volatilized mercury.

COAL-CONVERSION-PLANT WASTES AND EMISSIONS

Status of Potential Conversion Industry

The number and type of coal-conversion processes which will be used in the United States will depend, in part, on the scope of the newly developing national energy policy and on the need for clean fuels to assure the preservation and improvement of the environment.

A recent report (U.S. ERDA 1975) on synthetic fuel commercialization prepared by the U.S. Energy Research and Development Administration (ERDA) and the U.S. Department of the Interior recommended that coal-conversion effort be focused on the production of: (a) synthetic gas from coal, (b) synthetic petroleum from coal, and (c) synthetic utility and industrial fuels from coal. Because the coal-conversion processes

TABLE 1.19 Effects of SO_2 and HF Pollution on Foliage of a Tree at Billings, Montana (1973 foliage)

Parameter	Tree #2051	
	A*	B*
Fluoride (ppm)	117	19.4
Sulfur (ppm)	1500	1550
% Needle retention	74	79
% Healthy needles	8	33
% Total necrosis	11	9
% Tip burn	73	45
% Mottle	0	0
% Weevil	2	3
% Other pathology	6	3
Needle length (mm)	112.4	136.6
Needle cross-section area (mm^2)	2.99	3.54

* A = Side of crown facing Corette Steam Plant.
B = Side of crown facing away from Corette Steam Plant.

SOURCE: Gordon et al. (1976).

now being considered have not been built in commercial sizes in the United States, postulation as to the ultimate disposition of accessory elements from each coal-conversion process is mostly speculative and subject to refinement as more definitive data are obtained.

Coal-conversion processes require reducing conditions to convert coal to alternate hydrocarbon forms. Current approaches to coal conversion involve pyrolysis, solvent refining, hydrogenation, or production of synthetic gas. In pyrolysis, the coal is thermally decomposed in the absence of oxygen to coke, tars, light oils, combustible gases, and water. In solvent refining, the coal is solubilized using solvents such as methanol that add hydrogen to the coal and produce a liquid product containing low ash and sulfur. In hydrogenation processes hydrogen and coal react directly under increased temperatures to form either a liquid or gaseous product. Synthetic gas is produced using an oxidizing agent (air or oxygen) and steam to produce gas of varying Btu content, generally 100 to 1,000 Btu per standard cubic foot (scf).

While the above processes may require mining, preparation and pretreatment of coal, an in situ gasification process generates gas underground by the partial combustion of in-place coal.

With the exception of in situ gasification, all the coal-conversion processes involve the processing of coal at elevated temperatures and pressures in containment vessels.

Process Types

High-Btu Gasification (900 to 1,000 Btu/scf)

This process causes coal to react under pressure with oxygen and steam to produce a raw gas which is subsequently upgraded (methanated) to a high-Btu gas comparable in quality to natural gas. In the process, two major effluents result: solid ash or slag and liquid wastes from the scrubbing of the raw gas. Several liquid-waste streams are produced, each a potential conduit for accessory element distribution. Elemental sulfur is generally produced in commercial quantity from the raw gas.

Low- and Medium-Btu Gasification (150 to 300 and 300 to 400 Btu/scf)

Low-Btu gas from coal is produced in a manner similar to high-Btu gasification except that air is generally used rather than oxygen and there is no methanation step. When oxygen is used, a medium-Btu gas is formed, but is not followed by methanation that produces a high-Btu gas. The fuel is designed for use in nearby utility or industrial boilers, because, considering the lower heat value, low- and medium-Btu gas is not economical to transport more than a few miles. The low-Btu processes produce similar waste streams: dry ash, liquid wastes and airborne discharges. Again, elemental sulfur is usually a byproduct.

Liquid Fuels

Several hydrogenation processes are under development which use heat, catalysts and hydrogen to produce liquid fuels such as methanol, syncrude or gasoline. In these processes, too, solid- and liquid-waste streams are produced.

In Situ Gasification

Underground (in situ) coal gasification has been extensively used in the Soviet Union and tested on a more limited basis in Europe and the United States. While problems remain to demonstrate the process, production of 150 Btu/scf quality gas has been maintained on a limited basis. Accessory elements are found in the product gas as well as in air and liquid wastes.

Magnitude of the Problem

As currently envisioned, a coal-conversion plant, to produce 250 million standard cubic feet of pipeline-quality synthetic natural gas (SNG) per day, would burn 8 million tons of Illinois coal annually. In the process, about 2 million tons of solids would be generated as dry wastes with lesser streams of liquid and airborne wastes also generated. The large quantities of wastes which would be produced focus attention on their composition. Sixteen pounds of an element distributed in the above 8 million tons of coal would equal 1 part per billion of that element in the coal; 8 tons would equal 1 part per million. The significance of the presence of a given element, however, will depend on its toxicity, chemical characteristics, its affinity with other elements, and its dispersion.

Forecasts of the use of coal-conversion processes have consistently predicted that a major expansion will occur after 1990, with possibly no more than four or five major installations being operational by 1985. The first commercial SNG coal-gasification plant in the United States, for example, will not be operating before late 1981 at the earliest. Several other coal-conversion process plants, however, are in the early planning stage, and it is imperative that problems of handling accessory elements and fugitive compounds be identified promptly.

Composition of Solid Wastes

If predictions concerning the development of coal-conversion processes are realized, the late 1980s will see the production of increasingly large quantities of new kinds of solid wastes. The disposal of these solid wastes will be unprecedented in the United States and successful commercial-scale production of synthetic gas and oil by these processes will depend, in part, on the environmentally acceptable disposal or recovery of byproducts from the solid and liquid wastes.

Waste products from pilot-scale coal-gasification and liquefaction processes are now available for chemical and mineralogical characterization. It is clear, however, that many of these wastes will contain solid chemical components not originally present in the whole coal. As a consequence, minerals in the whole coal may have different solubilities from the minerals encountered in cleaning wastes. A listing of some coal-gasification processes, the general type of solid waste produced, and the predicted quantity in pounds per hour is given in Table 1.20.

Although work on coal-conversion solid wastes is new, limited studies have been conducted on the mineral and chemical nature of a few types. For the Synthane PDU gasifier, it was shown by Forney et al. (1975) that the greatest percentage of 16 selected trace elements occurred in the chars and dusts. Schultz et al. (1977) observed that Cu, Cr, Mn, Ni, Cd, and Pb concentrations were higher in the Synthoil centrifuge residue than in the feed coal; thus the residue was the primary sink for these elements.

Recent published results (Attari et al. 1976a,b) for residues from the Institute for Gas Technology's HYGAS process show that Ba, Co, Fe, Li, Mg, Mo, Ni, K, Sm, Si, Na, and Ti were almost totally retained in the residues of the two coals studied (Illinois No. 6 and Montana lignite). Others, such as Ca, Ag, and Sn, show a decrease in the Illinois No. 6 residues but not in the Montana lignite residue (Table 1.21). It was also found that moderate changes in temperature and pressure did not significantly alter the trace-element distribution. Thus, accessory element amounts in a process residue will be more

TABLE 1.20 Solid Wastes Produced by Several Coal Gasification Processes

Process	Type of Solid Waste	Quantity of Solid* (lb/hr)
BI - GAS	Water-quenched slag	68,400
CO_2 Acceptor	Water-cooled char/spent acceptor	496,800
HYGAS	Water-cooled lock-hoppers ash/char	138,900
Koppers-Totzek	Water-quenched slag	111,500
LURGI	Water-cooled ash locks	314,000
SYNTHANE	Dry-let-down fluid-bed char	362,200
U - GAS	Water-cooled venturi-throat char	86,400
Winkler	Water-cooled screw-conveyor char	372,500

* If individual values are used, the original reference (Magee, 1976) should be consulted to determine the original basis of computation.

SOURCE: Magee (1976).

TABLE 1.21 Summary of Institute of Gas Technology (IGT) Analytical Results for 38 Trace and Minor Elements in Feed and Residue Samples of Two Coals Hydrogasified in a Bench-Scale Unit

Element	Illinois No. 6 Bituminous				Montana Lignite		
	Feed	Pretreated Residue	Hydrogasified Residue	Loss	Feed	Hydrogasified Residue	Loss
	ppm	ppm	ppm	%	ppm	ppm	%
Sb	1.1	0.78	0.72	35	1.2	0.93	23
As	24	21	16	33	18	8.6	52
Ba	31	30	31	0	1,300	1,300	0
Be	1.0	0.85	0.76	24	0.98	0.76	22
Bi	1.1	0.94	0.54	51	0.72	0.41	43
B	200	190	180	10	85	61	28
Cd	0.89	0.56	0.21	76	0.72	0.33	54
Ca	3,500	2,800	2,300	34	17,000	17,000	0
Cl	2,300	1,500	590	74	180	95	47
Cr	15	15	15	0	14	11	21
Co	3.6	3.6	3.6	0	4.4	4.4	0
Cu	19	19	19	0	8.8	6.2	30
F	61	59	45	26	71	45	37
Ge	4.3	4.1	3.9	9	2.7	2.1	22
Fe	14,000	13,500	13,000	7	9,200	9,300	0
Pb	11	5.8	5.8	47	1.9	1.0	47
Li	33	33	33	0	5.8	5.8	0
Mg	570	600	580	0	5,800	5,700	2
Mn	48	44	39	19	8.9	8.5	4
Hg	0.12	0.025	0.0045	96	73	0.0075	99
Mo	7.0	6.9	6.8	3	2.1	1.9	10
Ni	15	14	14	7	23	21	9
N	10,400	10,400	2,400	77	9,200	1,500	84
K	1,700	1,700	1,700	0	340	330	3
Sm	0.74	0.74	0.74	0	0.51	0.50	2
Se	13	11	7.5	42	1.7	0.58	66
Si	20,000	20,000	20,000	0	13,000	12,000	8
Ag	0.10	0.069	0.036	64	0.24	0.23	4
Na	1,400	1,500	1,500	0	180	170	6
Sr	37	38	37	0	350	230	34
S	38,000	29,400	7,800	80	9,900	3,300	67
Te	8.1	6.3	4.8	41	0.42	0.24	42
Sn	2.0	1.5	1.0	50	1.9	1.8	5
Ti	770	770	750	3	320	340	0
V	17	15	14	18	67	54	19
Yb	0.56	0.55	0.52	7.1	0.36	0.32	11
Zn	49	42	36	27	13	9.5	27
Zr	35	33	35	0	25	22	12

SOURCE: Attari et al. (1976a).

closely related to the character of the coal than to changes in process conditions.

Studies of catalytic liquefaction also indicated that a major amount of trace metals remains in the filtered residue (Given et al. 1975). Filby et al. (1978) found a similar trend for the distribution of trace elements in the solvent-refined coal (SRC) process. Their general magnitudes of distribution, based on neutron activation analyses of composite samples collected over a 24-hour period from pilot-plant operations, are shown in Table 1.22.

The elemental composition for some 60 constituents in Lurgi ash and an H-Coal residue has been reported (Griffin et al. 1978). These data are summarized in Appendix Tables A1.14 and A1.15. The major constituents are Al, Ca, Fe, K, and Si. Large quantities of Mg, Mn, Na, S, and Ti are also present as well as significant quantities (10 to 1,000 parts per million) of the trace elements.

Compounds found in the Lurgi ash are similar to those usually associated with ash from coal-fired power plants. Those detected in the H-Coal residue samples included compounds having the composition of quartz, pyrrhotite, sphalerite, calcite, anhydrite, illite, kaolinite, and some expandable clay minerals. Thus, the established mineral relationships of compounds in the ash or residue in closed systems cannot be directly related to phases present in the liquefaction waste. Reactions of solid-waste compounds must be deduced from a thorough study of both the original coal mineral matter and mineral compounds found in the ash after coal conversion.

Liquid Effluents, Gaseous Emissions, and Byproducts

Liquid effluents, gaseous emissions, and byproducts such as tars, oils and other hydrocarbon mixtures are produced in relatively large amounts by coal-conversion plants. The basic chemical reactions that occur in coal-conversion processes are generally known (for a recent review, see Huffstetler and Rickert [1977]). Because the reactions take place in confined vessels, it is believed that coal-conversion processes will control accessory element emissions more effectively than present coal-utilization practices.

Emissions from coal-conversion and associated treatment units include sulfur (S_2, S_4, H_2S, SO_X, COS, mercaptans, thiophenes), nitrogen (NO_X, HCN, thiocyanates), particulate matter (debris, fines, ash, chars), trace elements, waste waters, organic compounds, spent catalysts, thermal effluents, carbon dioxide, and radioactive materials (Dailey 1977b).

Elements highly volatile at the temperatures and pressures of the conversion vessels are discharged with the raw gas, typically as sulfides (Jahnig and Bertrand 1976). These elements, which include sulfur as H_2S, are mostly scrubbed from the raw gas and enter liquor recovery streams. Some, such as Hg, As, Cd, Se, and Zn, will be reduced to metal in the presence of carbon. Hydrides of elements such as As, Sb, Se, Cl and F may be formed by reactions with hydrogen in the gas. Elements such as Fe, Ni or Co may form carbonyls with the carbon monoxide present. However, the distribution of many trace elements among coal-conversion emissions is not fully known (Dailey 1977b).

TABLE 1.22 Summary of Trace Element Data in SRC I Process Streams (Equilibrium Set 2)

Element	Process Fractions								
	Ground Coal	Solvent Refined Coal	Pyridine Insolubles	Wet Filter Cake	Light Oil	Process Recycle Solvent	Wash Solvent	Process Water	Effluent Water
Ti (ppm)	660^+	490	4480	<1500	2.50	15.0	1.8	<0.3	<0.2
V (ppm)	29.2^+	13.7	226	103	0.44	0.80	0.32	<0.001	0.009
Ca (ppm)	660^+	123	10200	10300	<12	9.7	<6	<10	9.6
Mg (ppm)	<2400	96.0	5290	4550	10.5	<8	7.2	<17	4.2
Mn (ppm)	35.7	14.2	219	147	<0.1	1.27	0.16	0.04	0.03
Al (%)	1.58	0.042	6.84	2.84	74**	41.6**	56.4**	0.40**	0.25**
Cl (ppm)	289	99.0	668	147	300	38.9	115	17.0	3.70
As (ppm)	20.1	2.27	388	3.24	2.85*	243*	68.6*	10.7*	<5*
Sb (ppm)	1.43	0.06	9.05	6.38	1.86*	9.20*	--	1.0*	0.66*
Se (ppm)	3.03	0.080	14.1	8.64	0.023	0.036	0.012	914*	0.37*
Hg (ppb)	114	46.7	497	33.8	3.40	<1	10.2	20.7	5.5
Br (ppm)	3.72	4.93	10.1	12.3	0.018	0.752	0.048	18.3*	<10*
Ni (ppm)	12.4	<2	170	142	0.04	0.22	<0.04	14.0*	10.0*
Co (ppm)	5.20	0.25	32.2	24.4	1.8*	37.6*	1.20*	0.43*	0.36*
Cr (ppm)	14.8	5.50	200	141	<5*	2.42	0.018	11.3*	10.1*
Fe (%)	2.38	0.026	13.7	9.37	0.30**	57.5**	7.0**	1.34**	0.41**
Na (ppm)	173	6.30	1040	710	0.04	1.18	0.33	5.10	<10
Rb (ppm)	11.8	0.21	76.7	54.1	<0.01	<0.02	<0.01	0.77**	1.36*
Cs (ppm)	0.91	<0.2	4.93	3.34	0.84*	1.53*	1.02*	0.04*	0.06*
K (ppm)	2030	2.27	11200	7600	0.20	<0.5	0.22	0.73	<1
Sc (ppm)	2.48	0.36	18.5	12.3	0.13*	24.5*	0.10*	0.12*	0.12*
Tb (ppm)	0.32	0.030	2.41	1.64	<0.1*	1.7*	<0.2*	<0.01*	<0.01*
Eu (ppm)	0.20	0.027	1.06	0.77	<0.001	<0.001	<0.001	0.012*	0.015*
Sm (ppm)	1.65	0.117	10.4	7.47	<0.01*	10.1*	0.15*	<0.1*	<0.1*
Ce (ppm)	20.8	0.36	131	94.6	<0.005	0.03	<0.004	<0.2*	6.5*
La (ppm)	6.56	0.09	37.4	25.9	<0.001*	9.30*	<0.001*	<0.7*	<0.01*
Sr (ppm)	158	<4	<74	271	<0.1	<0.2	<0.1	<0.02	<0.01
Ba (ppm)	62.5	<2	409	390	<0.1	0.18	<0.1	<0.02	<0.01
Th (ppm)	1.90	0.19	12.6	9.30	<0.001	0.015	<0.001	<0.04*	0.09*
Hf (ppm)	0.59	0.069	4.32	3.0	<0.001	0.004	<0.001	0.04*	0.02*
Ta (ppm)	0.17	0.05	1.07	0.81	<0.5*	3.20*	<0.4*	0.02*	<0.2*
Ga (ppm)	3.26	<1.5	13.1	10.3	<0.1*	34.3*	<0.1*	<0.004	<0.004
Zr (ppm)	79.0	6.4	422	373	<0.1	0.34	<0.1	0.02	0.02
Cu (ppm)	14.3	1.15	93.0	93.7	0.02	0.23	0.02	0.24	0.025

Note: *Values in parts per billion
**Values in parts per million
+Values for raw coal

SOURCE: Filby et al. (1978).

Likewise organic emissions from coal conversion are largely uncharacterized; however, nearly all products found in carbonization and coking streams may occur in intermediate-temperature gasification processes such as the synthane process. The multitude of organic constituents that may be present in the gas- and liquid-waste streams from coal conversion include naphtha, coal tar, oils, BTX (benzene, toluene, and xylene), product gases, and various potentially carcinogenic compounds and elements. Some of the latter are listed in Table 1.23 (Talmage 1977). Woodward, as referenced in the review by Dailey (1977b), states that similarities among the Synthoil synthetic crude oil, other syncrudes and petroleum crude oils indicate that much of the present petroleum technology is applicable to coal-derived syncrude processing. Little seems to be known of the fate of carcinogenic compounds in coal-conversion processes. Most atmospheric polycyclic aromatic hydrocarbon (PAH) compounds and polycyclic organic materials in the atmosphere are adsorbed to particulate matter, and conventional emission control such as water-spray flue-gas scrubbing for fly ash can reduce PAH emissions significantly (Hangebrauck et al. 1964 and Dailey 1977b).

Water requirements, water quality, and treatment for coal-conversion process waters were reviewed in detail by Dailey (1977b) and by Goldstein and Yung (1977). Table 1.24, from Goldstein and Yung, gives typical analyses for foul water from conversion reactors. It is highly contaminated with organics and ammonia, but it is probably low in metals. Water treatment for removal and recovery of organics and ammonia is described in these reports, but no information is given on the disposition of trace elements. Table 1.25, from Forney et al. (1974, 1975), shows results of trace-element determinations in process-condensate water from the Synthane gasifier. Attari et al. (1976a) examined the fate of trace elements in the Institute of Gas Technology's process development unit and HYGAS pilot plant and found significant losses due to volatilization regardless of coal-feed type or size of the gasification unit. They concluded that the elements so removed will likely concentrate in the quench and acid-gas scrubber, thus requiring a systematic recovery and disposal of the accumulated elements.

Determination of accessory elements in the tar produced from gasification plants shows relatively high concentrations of lead (50 parts per million) while oil samples indicate high levels of arsenic (30 parts per million). These concentrations raise concern as to the safety of the subsequent use of some tar fractions. Other samples from coal-liquefaction processes contain titanium on the order of 200 parts per million. The implications of increased amounts of accessory elements present in hydrocarbon byproduct streams dictate a need for thorough examination of the ultimate distribution of the accessory elements in byproducts as well as wastes. A further example is byproduct char; in the COED process, char produced amounts to 50 to 60 percent of the coal feed, which may contain large enough amounts of sulfur and other accessory elements to create an emissions problem if used as a fuel. However, emissions from coal-char combustion have not been investigated to any extent (Dailey 1977b).

TABLE 1.23 Carcinogens of Concern in Coal Liquefaction and Gasification Process Streams

Chemical classification	Compound	Phase	Remarks
Amines	Diethylamines	Gas	Potential source of nitrosamines from reaction with nitrogen oxides
	Methylethylamines	Gas	
Heterocyclics	Pyridines	Gas/liquid	
	Pyrroles	Gas/liquid	
Hydrocarbons	Benzene	Gas/liquid	
Phenols	Cresols	Gas/liquid	May be promoters
	Alkyl cresols	Gas/liquid	
Polynuclears	Anthracene	Gas	
	BaP[a]	Gas	
	Chrysene	Gas	
	Benzo[a]anthracene	Gas	
	Benzo[a]anthrone	Gas	
	Dibenzo[a,l]pyrene	Gas	
	Dibenzo[a,n]pyrene	Gas	
	Dibenzo[a,i]pyrene	Gas	
	Indeno[1,2,3-c,d]Pyrene	Gas	
	Benzoacridine	Gas	
Trace elements	Nickel	Gas	
	Beryllium	Gas	
	Cadmium[a]	Gas	
	Arsenic[a]	Liquid	
Organo-metallics	Nickel carbonyl	Gas	
Fine particulates	Sulfur particulates	Gas	May be a cocarcinogen
	Coke	Gas	
	Coal dust	Gas	

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[a] Potential mutagens or teratogens, based on Teratogen/Mutagen Sulfide, Registry of Toxic Effects of Chemical Substances, National Institute for Occupational Safety and Health.

SOURCE: Bridbord (1976) as referenced in Talmage (1977).

In Situ Gasification

Concentrations of trace species in low-Btu process gas produced by underground coal gasification (UCG) at the Hanna II project (Laramie Energy Research Center) have been reported. Those species identified include Na, K, Li, Ca, V, Hg, Pb, Cd, As, Se, NH_3, HCN, COS, and CS_2 (Fischer 1976). No commercial UCG plants exist in the United States but research is under way. It is reasonable to expect the damage to the environment by UCG will be comparable to conventional coal extraction techniques (Arthur D. Little, Incorporated 1975). Temporary disruption of the land surface is small for UCG, but UCG subsidence may be similar to that produced by underground coal mining. Moreover, UCG may lead to

TABLE 1.24 Typical Analyses of Foul Water from the Solvent-Refined Coal (SRC) Process and from Gas Plants

	Hygas and Lurgi Plants (mg/l)	Synthane and SRC Plants (mg/l)
BOD_5	13,000-18,000	about 30,000
COD	25,000-30,000	30,000-40,000
Phenol as C_6H_5OH	4,000-6,600	4,000-6,600
NH_3 as N	3,500-4,500	about 12,600*
HCO_3	about 13,000	about 4,000*
Sulfide as S	low	about 14,600*
Ca	about 20	about 20
Mg	about 15	about 15
Na	about 80	about 80
Cl	**	**
SO_4	low	low

* These numbers apply to SRC only. In the Synthane water these components are taken to be the same as in the Hygas water.

** Chloride concentration (ppm).

SOURCE: Goldstein and Yung (1977).

alteration of the dissolved-solids content and to contamination of ground water, which also occurs as a result of conventional mining. It is in this latter area that knowledge of the redistribution of accessory elements is lacking and for which additional research is needed. For well water in the vicinity of the underground gasification site near Gillette, Wyoming, Mead et al. (1977) found 70 inorganic elements and compounds, phenolic materials, dissolved organic carbon, and volatile organics to be present above background levels. However, all contaminants decreased rapidly with distance from the burn zone.

A recent symposium on in situ processing of coal (American Chemical Society 1977) contained 10 papers, indicating renewed interest in this method of coal gasification. Brandenburg et al. (1976) in summarizing the work at Hanna II reported that high resource utilization, flexibility, consistent gas quality, favorable economics and lack of clean-up problems have been demonstrated.

Areas of Limited Information

Subjects where limited information precludes a complete understanding of the ultimate disposition of accessory elements include methods of ash and sludge disposal in underground mines, in strip-mined areas followed by return of the overburden and reclamation, and in landfills that are subsequently buried.

The biological and health aspects of atmospheric and ground-water pollutants from coal-gasification products, especially those that may have been uniquely created by the reducing atmosphere, require considerable attention (Hildebrand et al. 1976, Herkes 1976, Gehrs 1977, Vaughan et al. 1975, and Braunstein et al. 1977).

In both liquefaction and gasification processes, sulfur contained in the coal is expected to be converted to hydrogen sulfide and recovered as elemental sulfur. Scrubbing operations will substantially remove the sulfur to the scrubbing-liquor streams. Carbonyl sulfide and carbon disulfide, which also occur, are resistant to conventional scrubbing methods and will require more attention during collection and disposal.

Nitrogen oxide emissions from both the nitrogen in the coal and the use of air in coal-conversion processes are subject to regulatory control. The technology developed for nitrogen oxide control from coal-combustion plants will be applicable to coal-conversion processes.

TABLE 1.25 Elements in Condensate from an Illinois No. 6 Coal Synthane Gasification Test

	No. 1	No. 2	Average (by weight)
Ppm:			
Calcium	4.4	3.6	4
Iron	2.6	2.9	3
Magnesium	1.5	1.8	2
Aluminum	0.8	0.7	0.8
Ppb:			
Selenium	401	323	360
Potassium	117	204	160
Barium	109	155	130
Phosphorus	82	92	90
Zinc	44	83	60
Manganese	36	38	40
Germanium	32	61	40
Arsenic	44	28	30
Nickel	23	34	30
Strontium	33	24	30
Tin	25	26	20
Copper	16	20	20
Columbium	7	5	6
Chromium	4	8	6
Vanadium	4	2	3
Cobalt	1	2	2
Run No.	162	163	164
Ppm:			
S	5,000	5,000	5,000
Total carbon	16,000	16,000	16,000
B	43	1,717	82
Cl	300	170	190
F	39	37	32
Na	6.6	6.8	5.4
Si	2.8	4.7	6.6

SOURCE: Forney et al. (1974, 1975).

Major quantities of the accessory elements will remain with the ash. Other than ash, the primary conduits for accessory elements will be the chars, the waste liquors, the streams that scrub the raw gas, and the byproduct streams. The scrubbing liquors will contain a wide variety of organic compounds, compounds similar to those produced by coke ovens and by petroleum refineries. Current control technology applied to these latter industries will apply equally to coal-conversion processes. With slight modification, many standard refining techniques will be applicable to the wash liquors and byproduct streams from coal-conversion processes (National Research Council 1977b).

The behavior of accessory elements in entering the natural environment will depend on climate, topography, and soil and rock character as well as on the physical and chemical properties of the elements themselves. Plans should be made now to test the first commercial coal-conversion plants as they become operational. Accurate estimates of emissions will not be available until that time. Environmental baselines should be measured prior to plant operation.

A careful assessment should be made of accessory element redistributions from coke-oven and oil-refinery operations because emissions from coal-conversion processes are anticipated to be similar in character. Studies of the biological and health impacts of accessory elements in ash, char, and liquid discharges from coal-conversion processes can best be made at the design stage.

SOLUBILITY OF ACCESSORY ELEMENTS IN COAL SOLID WASTES

Factors Influencing Solubility

The pH of the enclosing medium is one of the most important factors affecting the solubility of the accessory elements in coal solid wastes. Many coal wastes contain sulfide minerals that can oxidize and acidify water. Most of the heavy metals in solid wastes disposed of in acidic waters in strip or underground mines are more soluble than wastes disposed of under neutral or alkaline conditions. This fact may be of value when considering potential byproduct recovery.

The oxidation potential (Eh) is also an important factor affecting the solubility of minerals. Mineral stability is a close function of both Eh and pH (Garrels and Christ 1965). When solid wastes are buried underground or in water-saturated materials, negative Eh, anaerobic (oxygen-deficient) conditions usually develop.

The chemical form of the accessory elements in both coal-cleaning and conversion wastes has an important bearing on solubility. Current information on fly ashes and slags produced in coal-fired furnaces may not be pertinent when considering conversion waste because the conversion products are produced at high temperatures and pressures in a reducing atmosphere rather than an oxidizing one. Significant alterations in chemical form of accessory elements may result and these can affect solubility and, hence, the potential pollution hazard.

Thus, data on the solubility, transport and toxicity of accessory elements in coal wastes are important in the assessment of the environmental aspects of coal utilization. Moreover, it is conceivable that large quantities of solid waste generated from gasification and liquefaction processes and coal-cleaning plants may be usable as "ores" in the future.

Solubility and solubility rates of many types of wastes can be affected by their physical properties, such as particle size and internal surface area. The particle size is at least partly a function of the process by which the waste was produced, whereas the internal surface area may be either an innate property of the material itself or a function of the process, as in changes brought on by high temperature.

In addition to the foregoing, many of the trace elements form stable complexes with inorganic ions or soluble organic compounds. This may result in orders-of-magnitude solubility increases, above those concentrations predicted by solubility-product calculations, for the most stable solid phase (Vaughan et al. 1975).

The mobility of soluble ions and compounds in the environment, as water passes through earth materials into ground water or surface streams and lakes, depends upon the system's texture, structure, and adsorption capacity (cation and anion exchange capacity). Of primary importance are the kinds and amounts of clay, hydrous oxides, organic matter, competing ions in solution, and, perhaps, the changes brought about by microorganisms in the system.

A recent article (Chemical and Engineering News 1977) emphasizes the fact that microorganisms are responsible for converting inorganic trace metals to organometallic compounds along common pathways. By fixing methyl groups onto the metals, bacteria render them less polar and more soluble in the cell's organic phase.

Environmental conditions can significantly affect the trace-metal biological cycle. According to the article in Chemical and Engineering News, metals such as Pb, Tl, Se, Pd, and Hg (elements with high oxidation potentials) are methylated under aerobic conditions. Metals with low oxidation potentials such as tin, selenium, and arsenic are methylated under acid conditions, and chromium is methylated under reducing conditions. Thus, particular environments would be much more conducive to creation of potential trace-metal hazards and overloading of the biologic cycle. A knowledge of environmental conditions, especially the Eh conditions, and the trace metals present should aid in predicting where these areas are most likely to occur.

On the other hand, organic wastes such as phenols are readily degraded by microbes, and as much as 85 percent of the polycyclic aromatic hydrocarbons (PAH) can be degraded by common soil bacteria (Dailey 1977a).

Soil components can serve as a reservoir or sink for many accessory elements. Even though immobilized by adsorption, elements may still be partly available for plant uptake and redistribution due to slow dissolution or microbial action.

Baseline Data

In order for the environmental effects of the redistribution of soluble accessory elements to be accurately evaluated, it is necessary, wherever possible, to determine baseline amounts of those elements in pristine environments. One of the most effective ways of accomplishing this is through the analysis of area ground water and stream sediments. The stream sediments preserve a history of past events buried in the sediment column and reflect the present environment in suspended and surficial sediments (Shimp et al. 1971, and Frye and Shimp 1973). Studies are now being conducted on stream sediments (McNeal 1976, and Keith et al. 1976) and ground water (Feder and Saindon 1976) in western coal-producing regions. These and other similar studies (Morgan 1978) provide unique opportunities to develop the best data base ever obtained for the evaluation of the impact, both beneficial and deleterious, of coal mining and combustion on the environment.

Coal-Cleaning Wastes

Because of the complexity of factors responsible for solubility, mobility, and attenuation of accessory elements contained in coal solid wastes, most published results are specific and "after the fact" rather than predictive. That is, results for soluble pollutants are obtained for a drainage area after disposal. For example, Martin (1974) collected drainage effluents from coal-cleaning wastes in Illinois, Pennsylvania, Kentucky, West Virginia, and Indiana and determined pH, conductivity, sulfate, Fe, Al, Mn, Ca, Mg, Na, K, Cu, Zn, Ni, and Pb in many of the samples. The general observation made for these results by Wewerka et al. (1976) is that total acidity and ion concentrations (trace elements and sulfate) are only casually related to acidity of the effluents. This implies that total dissolved material from the refuse piles is also dependent upon local conditions such as rainfall, particle size, mineralogy, and area drainage patterns. Further, Martin's study indicated that relatively high concentrations of dissolved ions can occur in effluents from nonacidic as well as acidic wastes. Other long-term studies by Vimmerstedt and Struthers (1968) and Curtis (1972) on weathering of coal-cleaning wastes have produced results similar to those of Martin.

It is well known that most western coals usually contain smaller amounts of pyrite than do coals of the interior and that their coal-cleaning wastes are generally nonacidic. McWhorter et al. (1974) studied coal refuse from two locations in the southern Rocky Mountain Region. For runoff or leachate, the total salt content was lower, pH was higher and concentrations of metallic elements were lower compared to acid leachates. Nevertheless, problems from western coal spoils are becoming evident. A chemical comparison of water in spoil material to undisturbed ground water in the Northern Powder River Basin, Wyoming, (Van Voast et al. 1975) suggested changes that might be expected in the western coal-bearing areas. Manganese and nitrates appeared to be strongly enriched in spoil water over that in typical ground water, but calcium, magnesium, sodium, potassium, silica, chlorine, sulfate, and total dissolved solids may also be substantially elevated. A similar enrichment is also apparent when compared to shallow ground water from the Northern Great Plains (Feder and Saindon 1976). Large amounts of sulfate suggest oxidation of pyrite in the spoils. Little is known of trace-element mobilization during weathering of coal-mine spoils, although there appears to be a general tendency for many trace metals to be more soluble in acid, oxidizing solutions.

Solubilities of 18 elements in flue-gas desulfurization (FGD) and fluidized-bed combustion (FBC) wastes, including aqueous effluent from the coal-ash pond, are given in Table 1.26 (Battelle Columbus Laboratories 1977). Underlined values are amounts that exceed or could exceed U.S. EPA public water supply standards. These data indicate that some pollution problems associated with trace elements in the leachates are likely to be encountered. Rosshoff et al. (1977) studied the solubility of untreated and treated FGD sludge. (Treated FGD sludge has undergone chemical treatment to reduce its permeability and solubility properties.) Results of these tests are given in Table 1.27 and Figure 1.2. They show an initial high rate of leaching from FGD sludge. This rate decreases rapidly until after the equivalent of 3 to 5 pore volumes of liquid have percolated through the sludge, at which time the rate of decrease becomes very low or constant. The initial high rate is believed to be caused by a flushing mechanism; the low rate is probably a consequence of the solubility of crystalline phases. The chemical fixation treatment resulted in leachate with amounts of major elements about one-half those of untreated sludge; however, chemical treatment did not alter the solubilities of lead, zinc, and selenium in treated FGD sludge.

Knowledge of coal-ash solubility and methods for environmentally acceptable disposal of coal ash is still incomplete. Characteristically, ashes produced by coal-combustion processes are glassy, partly fused, and contain inclusions of iron oxide, magnetite, carbon particles, calcite, other crystalline materials, and trace elements as oxides. Application to field conditions of laboratory leaching studies involving coal ash and conversion wastes is always somewhat uncertain. Laboratory results for coal ash indicate a rather rapid leaching occurs for some accessory elements but it is uncertain whether this is a limited surface phenomenon or whether the entire ash deposit is subject to leaching (Lagarius 1977).

The Tennessee Valley Authority (TVA) has characterized waste-water effluents from coal-fired power plants since 1968. Recently, this work has involved the characterization of ash-pond effluents (Chu et al. 1976) to obtain data on the solubility properties of various coal ashes under different natural conditions. In addition, the research has focused on reuse of the ash-pond effluent. This aspect of the work is covered in the section below (Disposal and Attenuation of Accessory Elements).

Both bottom ash and fly ash are generally disposed of as a water slurry in settling ponds or trucked directly and dumped in strip-mined pits. The Tennessee Valley Authority operates ash ponds that receive fly ash, bottom ash, or both. Specific data on the chemical characteristics of ash ponds are summarized in Appendix Table A1.16. The pH of pond effluents ranges from 3.3 to 12; half of the effluents are alkaline. The acidic or alkaline characteristics depend on the content of sulfur trioxide and alkaline metal oxides in the ash materials and on the buffering capacity of the water used for sluicing. Factors that affect the ash characteristics include the source of the coal, the method of firing, the ash-fusion temperature, and the efficiency of equipment for collecting fly ash. In most plants, the

TABLE 1.26 Trace Metals in Ash, FGD Sludge Pond, Liquors/Supernatants, and FBC Ash and Spent Stone

	Ash Pond		FGD Sludge Pond		FGC Sludge Liquors		FBC Ash Leachates		FBC Spent Stone Leachates		EPA Proposed Standards Public Water Supply Intake
	Mean	High	Mean	High	Mean	High	Mean	High	Mean	High	
pH	10.9$^{(a)}$	12.5	8.9	9.7	7.4	9	11.4	12.2	12.16	12.5	5 to 9
Antimony	0.017	0.33	0.021	0.035	-	-	-	-	<0.3	<0.3	-
Arsenic	<0.036	0.084	<0.011	0.03	<0.068	0.20	0.68	2.5	5.0	5.0	0.1
Barium	8.24	40	0.866	2.0	-	-	-	-	-	-	-
Beryllium	0.0011	0.003	0.002	0.002	<0.041	0.18	-	-	<0.01	<0.01	-
Boron	3.66	16.9	3.286	6.3	-	-	0.39	0.61	0.37	0.83	1.0
Cadmium	<0.0031	<0.01	<0.0012	0.002	0.038	0.10	0.0025	0.01	<0.1	<0.2	0.01
Chromium	<0.267	1.0	<0.0043	0.011	<0.087	0.21	ND	<0.1	<0.1	<0.1	0.05
Copper	<0.031	0.092	<0.027	0.045	<0.070	0.20	-	-	<0.1	<0.1	1.0
Fluorine	4.88	17.3	15.93	31.5	-	-	-	-	-	-	-
Germanium	<0.01	0.01	<0.013	0.02	-	-	-	-	-	-	-
Mercury	0.0033	0.015	0.008	0.001	<0.045	0.12	-	-	-	-	0.002
Lead	0.0088	0.024	0.005	0.0061	0.072	0.18	1.3	2.5	<0.92	2.4	0.05
Manganese	<0.002	<0.002	<0.002	<0.002	-	-	-	-	<0.05	<0.05	-
Molybdenum	0.169	0.69	0.066	0.075	-	-	9.7	17	<5.8	12	-
Nickel	<0.037	<0.05	<0.05	<0.05	-	-	-	-	<0.1	<0.1	-
Selenium	<0.10	0.47	0.023	0.045	<0.75	2.5	-	-	-	-	0.01
Vanadium	<0.12	<0.2	<0.1000	<0.1	-	-	-	-	<0.05	<0.05	-
Zinc	<0.055	<0.19	<0.0270	<0.052	0.14	0.30	0.028	0.08	<0.4	<0.4	5.0
Samples	5		5		5		4		4		

NOTE: Except for pH, all concentrations are in parts per million.

(a) Underline indicates value higher than EPA and WHO standards. Underlined "less than" values should not be interpreted as being known concentrations in the samples that exceed EPA standards.

SOURCE: Data compiled by Battelle from information supplied by Aerospace Corporation, R. Stone and Company, Westinghouse Research Laboratory, and the U.S. Environmental Protection Agency.

TABLE 1.27 Chemical Constituents in Leachate from Untreated and Chemically Treated Flue-Gas Desulfurization Waste after 1 and 50 PVD* (Concentrations in mg/ℓ)

Chemical Constituent	Untreated Waste		Treated Waste	
	1st PVD	50th PVD	1st PVD	50th PVD
Arsenic	0.02	0.004	0.015	<0.004
Beryllium	0.01	<0.004	0.008	<0.002
Cadmium	0.015	0.002	0.02	0.002
Chromium	0.045	<0.003	0.06	0.003
Calcium	0.045	0.010	0.025	0.005
Lead	0.25	0.010	0.15	0.03
Mercury	0.0005	<0.00005	0.0007	0.0002
Selenium	0.055	0.006	0.040	0.008
Zinc	0.65	0.04	0.27	0.03
Chloride	2,600	100	600	75
Fluoride	4.0	0.8	1.1	0.4
Sulfite	50	30	35	20
Sulfate	6,500	1,200	3,500	450
Total Dissolved Solids	10,000	2,200	6,000	1,000
Chemical Oxygen Demand	10	6	7	4
pH	6.6	5.5	6.8	8.0

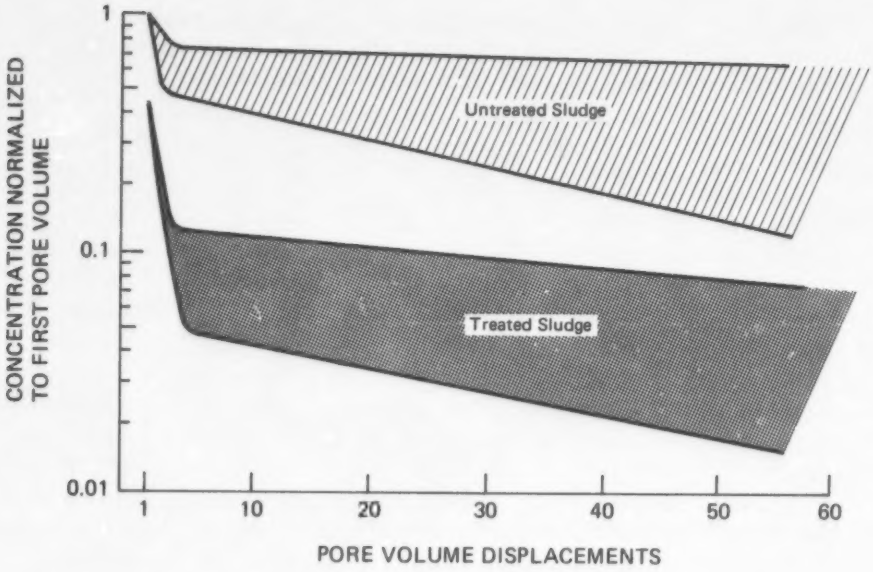
*PVD = Pore volume displacement

SOURCE: Rosshoff et al. (1977).

pyrite-rich material, which is removed from the coal before combustion, is also sluiced to the ash pond. Metallic and sulfuric compounds are released into the sluice water, depending on their bonding with the solids, their chemical form, exposure to oxidation, and the chemical properties of the water used for sluicing.

For the plants that use pulverized coal, pH of ash-pond effluents is mainly affected by the source of coal. In general, ash-pond effluents from plants that receive coal from western Kentucky and southern Illinois are alkaline, while those from plants that receive coal from eastern Tennessee, eastern Kentucky, and Virginia are neutral or acidic.

Of the principal components in fly ash (Table 1.28), calcium, sulfur, potassium, and sodium oxides were released readily into the sluice water independent of the pH level. Magnesium oxide and silica were not released into ash sluice water of alkaline pH. Iron and titanium oxides were not released into ash sluice water of either neutral pH or alkaline pH. Aluminum oxide was released only slightly into the alkaline sluice water. Concentrations of calcium and sulfate built up rapidly in all recirculated ash sluice water. Supersaturation



SOURCE: Rosshoff et al. (1977).

FIGURE 1.2 Curves showing concentrations of leachate total dissolved solids as a function of pore volume displacement in treated and untreated slud[illegible]hese curves are typical for Ca, Na, Cl. and SiO_4 ions.

of calcium sulfate, calcium carbonate, and magnesium and silica compounds may occur in recirculated systems. Precipitation, once started, can proceed quickly and can rapidly increase boiler-tube scaling. The decreasing order of trace-metal concentrations, resulting from leaching from two samples of fly ash after numerous cycles, was B > Ba > Al > Cr > Zn > Ni > Cu > Se > As, in alkaline ash sluice water, and B > As > Zn > Mn > Ni > Ba > Se > Cu > Cd, in neutral ash sluice water. Several trace metals, such as As, B, Ba, Cd, Cr, Mn, and Se, may cause water quality problems in the discharge of untreated recirculated ash sluice water.

Natusch et al. (1977) found that solubilities of many trace elements in fly ash are directly related to the solvent used and to an element's tendency to be concentrated in the particle's surface layer (1,000 Å). In Table 1.29, the elements Cd, Co, Li, Mn, P, Tl, and Zn predominate in the surface layer of the fly ashes studied and exhibit substantial aqueous extractability. Natusch et al. indicated that these elements may be largely available to the external environment when fly ash is subjected to weathering.

Theis and Wirth (1977) report that alterations in pH of the solution and trace-metal associations with amorphous oxide sinks which coat fly-ash particles are particularly important, the solution acting as an aqueous acidic component and the oxide as a specific sorption medium for many trace metals. With the exception of As, desorption of trace metals from fly-ash surfaces decreased with increasing pH, but even at neutral pH values significant fractions of Cd, Ni, Pb, and As may be released.

Coal-Conversion Wastes

Little published information is available on solubilities of accessory elements in the various coal-conversion solid wastes. Data obtained by Griffin et al. (1978) indicated the kind of laboratory results expected from Lurgi ash. Of some 60 constituents measured in residues of three coals gasified in the Lurgi plant at Westfield, Scotland, which were equilibrated in aqueous solutions at various pH values, about 30 were present in amounts that could present an environmental problem. The remainder occur at such low levels that, even if completely soluble, would not constitute a problem. Of the approximately 30 constituents that might be a potential problem, 21 were sufficiently soluble to produce concentrations exceeding water quality levels recommended by EPA. The 21 potentially troublesome constituents and the range of amounts measured for the three Lurgi ashes are summarized in Table 1.30. Eight constituents--B, Ca, K, Mn, NH_4, Pb, SO_4, and Sb--have been identified as being constituents that require further study because

TABLE 1.28 Chemical Composition of Dry Fly Ashes Used for Ash-Pond Recirculation Study

Constituent	Plant E	Plant J
Percent		
Alumina (Al_2O_3)	18.52	31.19
Barium Oxide (BaO)	0.22	0.16
Calcium Oxide (CaO)	5.74	1.82
Chloride (Cl)	0.25	0.35
Iron Oxide (Fe_2O_3)	20.79	8.76
Magnesium Oxide (MgO)	1.23	1.53
Potassium Oxide (K_2O)	3.37	4.34
Silica (SiO_2)	46.28	49.70
Sodium Oxide (Na_2O)	0.66	0.32
Sulfur Trioxide (SO_3)	1.55	0.40
Titanium Oxide (TiO_2)	1.07	1.27
Micrograms/gram		
Arsenic	55	170
Boron	1,800	400
Cadmium	6	<2
Chromium	90	140
Copper	78	170
Lead	75	100
Manganese	410	220
Mercury	0.1	0.42
Nickel	100	100
Selenium	6	8
Zinc	540	280

SOURCE: Chu et al. (1976).

TABLE 1.29 Estimated Surface Concentrations and Aqueous Extraction Efficiency of Elements in Fly Ash

Element	Solids Bulk Concentration (μg/gm)	Estimated Surface Concentration in 1,000 Å Layer (μg/gm)	Percent Extracted (25°C, 48 hours)
Fe	92,400	84,000	0.7
Si	110,000	21,000	0.1
Ti	4,700	9,600	1.5
Mg	12,300	9,800	0.6
Ca	<12,500	21,000	<1.3
Na	< 5,200	35,600	<5.2
K	38,800	103,000	6.0
Li	202	4,400	17.0
Pb	620	2,700	3.4
Tl	28	920	25.0
Cr	400	1,400	5.7
V	380	760	3.9
P	600	4,100	11.0
Mn	310	2,900	35.0
Zn	1,250	14,600	22.0
S	7,100	252,000	36.0
As	600	1,500	4.1
Co	65	440	18.0
Cd	24	700	19.0
Sb	30	95	2.1
Ba	770	240	0.2

SOURCE: Natusch et al. (1977).

their concentrations exceeded the recommended water quality levels at all pH levels in the equilibrated solutions. The remaining 13 constituents usually exceeded recommended levels when the solutions are quite acid. Discharges of these constituents at the levels found in this study could cause some environmental degradation and some form of waste-water treatment could be necessary.

DISPOSAL AND ATTENUATION OF ACCESSORY ELEMENTS

The disposal of wastes produced from coal-combustion and conversion processes may affect the quality of local surface- and ground-water systems. Present disposal practices for dry ash include burial in strip-mined areas and covering with overburden, followed by surface reclamation. Slurried wastes may be taken to disposal ponds, where the water is decanted and the sludge covered with soil. Alternatively, the disposal ponds may be dredged periodically for the partly dried wastes, which are then taken to disposal sites for burial.

A potential exists for degradation of ground water if the disposal areas are subject to seepage or are in proximity to aquifers in areas where ground-water movement prevails. Leaching of some elements in the ash occurs if exposed to percolation. Leachates may be diluted only slightly because of limited mixing of ground-water flow. To isolate leachates from local ground-water sources, proper site selection must be made. Ash may be deposited among naturally occurring impervious geological materials or in artificially prepared sites that minimize seepage.

TABLE 1.30 Summary of Constituents Contained in 10 Percent Aqueous Slurries of Lurgi Ashes Exceeding Recommended Water Quality Levels

Constituent	Solubility from Ash			Water Quality Levels Recommended by EPA
	Ill. #5	Ill. #6	Big Sky	
	mg/l			
Al	N.D.-128	N.D.-132	N.D.-510	0.1
B*	5.0-10.0	3.0-8.0	19.8-60.7	0.75
Ca*	410-1060	290-570	210-2050	50
Cd	N.D.-0.13	N.D.-0.06	N.D.-0.06	0.01
COD	2-86	2-140	N.D.-110	50
Cr	0.02-0.10	N.D.-0.16	0.01-0.20	0.05
Co	N.D.-0.27	N.D.-0.19	N.D.-0.23	0.05
Cu	0.02-0.30	0.01-0.73	N.D.-0.54	0.2
F	—	—	0.3-9.9	1.0
Fe	0.04-560	0.06-880	0.01-670	0.3
K*	29-44	26-61	8-34	5.
Mg	—	—	0.9-440	50.
Mn*	0.01-27.5	0.11-3.8	0.02-28.0	0.05
Mo	—	—	N.D.-0.8	0.01
NH_4*	3-16	8-17	13-25	0.02
Ni	0.01-1.37	—	—	1.0
Pb*	0.1-0.2	N.D.-0.2	N.D.-0.4	0.03
PO_4	—	—	N.D.-2.38	0.05
SO_4*	492-670	338-943	295-585	250.
Sb*	0.2-0.9	0.2-0.6	0.3-1.3	0.05
Zn	0.01-110	0.01-20	N.D.-1.5	0.2

*Highest Pollution Potential

N.D. = not detected

SOURCE: Griffin et al. (1978).

Earth Materials

The attenuation of trace elements by earth materials has received some attention. Among such studies are those of Fuller et al. (1976) and Griffin et al. (1976, 1977), which are concerned with soil or clay attenuation of various constituents in municipal landfill leachates. Although not directly related to coal, these studies have developed criteria for predicting migration trends of certain potentially hazardous constituents through soils. Fuller (1977) summarized the literature for 12 constituents, which he grouped with respect to mobility in soil under aerobic conditions (Table 1.31). The same publication contains results of studies on the relative mobility of

TABLE 1.31 Relative Mobility of Twelve Constituents in Soils (Aerobic Conditions)

Mobility Class	Element	Comments
I.	Relatively mobile	
	Cyanide - CN^{1-}	Not strongly retained by the soil.
	Selenium - $HSeO_4^{1-}$ & SeO_3^{2-}	Not strongly retained by the soil, at normal pH levels.
II.	Moderately mobile	
	Iron	Absorbed more strongly by the soil in the order of $Cu^{2+}>Pb^{2+}>Zn^{2+}$ Fe^{2+}. Stability for complexes of any given type should be increasing in the order of Fe>Zn>Pb>Cu.
	Zinc	
	Lead	
	Copper	
	Beryllium - Be^{2+}	(Chemistry in soils probably similar to aluminum.)
III.	Slowly mobile	
	Arsenic - $H_2AsO_4^{1-}$	Mobility similar to phosphorus.
	Cadmium - Cd^{2+}	Forms insoluble precipitates in oxidizing conditions.
	Chromium - Cr^{3+} (or Cr^{6+})	Forms insoluble precipitates in oxidizing conditions.
	Mercury - Hg^{2+}	Retained in the surface layer of most aerated soils.
	Asbestos - $< 2\mu$	Particles less than 2μ are retained in surface layer of soils like clay.
IV.	Immobile	
	Asbestos - $> 2\mu$	Particles $> 2\mu$, or greater than clay size, are retained on the surface of soils.

SOURCE: Fuller (1977).

eight constituents in soils under anaerobic conditions and using landfill leachate as the transporting medium (Table 1.32).

Griffin et al. (1976, 1977) studied the effectiveness of clay liners in attenuating pollutants. They found that Cl, Na, and water-soluble organic compounds (COD) were relatively unattenuated by passage through columns of clay; K, NH_4, Mg, Si, and Fe were moderately attenuated; and the metals Pb, Cd, Hg, and Zn were strongly attenuated by even small amounts of clay. Concentrations of Ca, B, and Mn were markedly higher in the effluents than in the original leachate. The potential usefulness of clay materials as liners for waste disposal sites depends to a large extent on the pH of the leachate solutions and on ionic competition during the ion-adsorption process. Adsorption of cationic heavy metals--Pb, Cd, Zn, Cu, Hg, Cr^{3+}--was found to increase as the pH increased, while adsorption of the anionic heavy metals--Cr^{6+}, As, and Se--decreased as the pH increased. The presence of leachate reduced by as much as 85 percent the amounts of the cationic heavy metals removed from solution, whereas leachate had relatively little effect on the amounts of the anionic heavy metals removed by the clays. It was concluded that removal of the heavy-metal cations from solution is primarily a cation exchange-adsorption reaction affected by pH and ionic competition, whereas removal of the heavy-metal anions is primarily an anion-adsorption reaction in which the monovalent ion is the predominant one being adsorbed. Precipitation of the heavy-metal cations in leachate was an important attenuation mechanism at pH values of 5 and above. No precipitation of the heavy-metal anions was detected in the pH range 1.0 to 9.0.

TABLE 1.32 Relative Mobility of Eight Constituents in Landfill Leachate Through Soils (anaerobic conditions)

Soil Series	Element in Leachate
Acid Soils	
Ava	Zn, Cd, As, Cr, Se, Cu Be Pb In order of decreasing mobility →
Kalkaska	
Wagram	
Davidson	
Molokai	
Chalmers	
Neutral to Alkaline Soils	
Anthony	Cr, As, Se, Cd, Be, Cu Zn Pb In order of decreasing mobility →
Fanno	
Mohave (limy)	
Mohave	
Nicholson	

SOURCE: Fuller (1977).

Water Reuse

Most coal ashes are collected at coal-fired power plants and sluiced to settling ponds for disposal. Small amounts are disposed of in landfills or recycled for use in special aggregates for such purposes as roadway and construction materials. Economy is the main advantage of ash-pond disposal over dry disposal. Ash ponds also minimize dust problems and are simple to operate. The water requirements for sluicing coal ashes are generally high, ranging from 1,200 to 40,000 gallons of water per ton of fly ash and from 2,400 to 40,000 gallons per ton of bottom ash (Chu et al. 1976). Meeting the effluent guidelines of 1983 (U.S. EPA 1974a) for water used to transport bottom ash may require water reuse. Thus, it is necessary to determine if the water quality of ash-pond effluents is sufficient to allow reuse for particular applications (Chu et al. 1975).

Four schemes for reuse of coal-ash-pond effluent have been considered in detail by Chu et al. (1976). In their view, the applicability of these schemes to specific sites needs further evaluation. Some factors needing evaluation are water-flow balances between the waste-water sources and the other power-plant operations that require water, the number of allowable cycles of sluicing water without causing problems with plant operation, the most economical waste-water reuse or recycling as opposed to other possibilities (such as dry disposal of fly ash), and the ultimate fates of several trace metals. Bench-scale and pilot-scale studies and demonstration projects are necessary to provide such evaluations.

Other Disposal Methods and Acid Mine Drainage Treatment

Other methods to attenuate the soluble constituents of coal wastes are being tested. Chemical fixation is a process that converts waste sludges into a relatively insoluble material with physical characteristics similar to concrete or clay. The effectiveness of this method has been estimated by Rosshoff et al. (1977). Generally, the total of dissolved solids passing through the subsoil is lower by a factor of 100 for chemically treated waste in landfills than for untreated waste in ponds. Nevertheless, protection of the environment, especially ground water, is best assured only through appropriate disposal site management techniques. In this connection, FGD sludge is thixotropic even after dewatering, and it is unsuitable for landfill without additives or chemical fixation (Argonne National Laboratory 1977).

Consideration has also been given to lining disposal ponds with flexible or nonflexible plastic liners of various kinds to provide a physical barrier that prevents seepage into ground or surface waters. Their effectiveness is dependent upon aging and chemical interaction characteristics.

Traditionally, the source of pollution from coal storage or refuse piles has been attributed to iron salts and sulfuric acid produced from oxidation of pyritic minerals contained in the refuse (for example, Singer and Stumm 1969, Smith et al. 1969, and Jones and Rugari 1969). Garrels and Thompson (1960) concluded that the rate of oxidation of pyrite was chiefly a function of oxidation-reduction potential (Eh) and independent of total iron content. There is also some evidence that oxygenation of Fe^{2+} can be affected by the catalytic responses of trace constituents such as copper (Stauffer and Lovell 1969).

Neutralization of acid mine drainage (AMD) has been practiced for years and may have broader application to accessory element attenuation than for just iron and raising pH. Recently Wewerka et al. (1976) reviewed the literature on AMD. (Table 1.33 is their summary of the methods employed.) Wewerka et al. have pointed out that the water-treatment methods are designed primarily to neutralize solution acidity by the addition of lime or limestone. However, because raising the pH has been found to be very effective in reducing trace-element concentrations in some leachates (Griffin et al. 1977), it may also accomplish the same thing for acid drainage from coal-refuse piles. At the same time its effectiveness might be improved through an oxidative treatment of the effluent. However, it is important to note that the fate of many trace elements in such processes has not been determined and that each treatment needs to be tailored to the drainage composition.

A review (Argonne National Laboratory 1977) of the composition of treated (lime-neutralized) AMD indicated that after neutralization relatively high amounts of Fe, Al, Mn, and Zn (1 to 10 parts per million) remain in solution or are transported as colloids. The latter can form during the neutralization process as a result of the precipitation of hydroxides, which remain in suspension unless further treatment such as filtration is effected.

TOXICITY TESTS

Specific regulations and criteria for the disposal of coal solid wastes have not been finalized. U.S. Public Health Service Standards for water quality and proposed standards for public water supply intake are

TABLE 1.33 Methods for Preventing or Controlling Acid Drainage from Coal Refuse Matter

Preventative Measures
Control of air influx
Control of water influx
Disposal in underground or strip mining sites
Treatment Methods
Neutralization
Flash Vaporization
Ion Exchange
Reverse Osmosis

SOURCE: Wewerka et al. (1976).

frequently used for comparison with amounts of elements in waste effluents (see Tables 1.26 and 1.30). In addition to inorganic constituents, water-soluble organic compounds may occur in the effluent from some coal-liquefaction wastes. If so, these need to be included in any evaluation of disposal hazards. However, neither standard laboratory nor field tests have been developed for assessing solubility, mobility, and toxicity of coal wastes, all three of which comprise the total environmental hazard.

One type of screening test may be applicable. Fish, for example, fathead minnows, can be propagated in the laboratory and used to determine the biological toxicity (total) of water-soluble constituents from coal solid wastes of various types. These studies are performed under controlled conditions in an environmental chamber using procedures such as those suggested by EPA (1975b). Preliminary results indicated some toxic effects from coal-conversion leachates and extracts, although the exact composition of these leachates and extracts has not yet been identified. Such tests are rapid and take into account both the solubility of the waste being tested and the synergistic effects of complex solutions. They have the disadvantage of being unable to discern long-term chronic effects of low concentrations.

The toxicity of 35 trace elements in "coal to fresh water biota" have recently been summarized from 313 references and compiled into a very useful data base (Cushman et al. 1977).

What appears to be an important new concept--multimedia environmental goals (MEGs)--has been published in two volumes by Cleland and Kingsbury (1977). MEGs are described as levels of significant contaminants (in ambient air, water, or land, or in emissions or effluents conveyed to the ambient media) that are judged to be (1) appropriate for preventing certain negative effects in the surrounding populations or ecosystems, or (2) representative of the control limits achievable through technology. MEGs are to be projected for more than 650 compounds and elements and, when further developed, they may become exceedingly useful in helping to assess pollution hazards associated with the redistribution of accessory elements from coal utilization. A wealth of background information for each chemical substance is supplied. Included, for example, are characteristic functional groups; preferred names, synonyms and chemical formulas; physical appearance; structure; valence states and ionic species; occurrence; compounds; toxic properties and health effects; and regulatory actions.

ECONOMIC IMPLICATIONS

Accessory elements in coals have economic implications because they create environmental problems in mining, processing, and utilization that may be detrimental to human health. Society may bear the costs of lessening these damages and, because perfect control may be technically impossible or inordinately expensive, it may also bear the cost of any residual damage. Accessory elements have mineral or chemical value for the environment in appropriate redistribution and some commercial value if recovered in sufficient quantities. Therefore, the economics of accessory element recovery is also of interest.

The costs (damages) of element collection or disposal can often be measured directly. For example, the capital cost of a control system gives a direct measure of many expenses. In other cases, only major costs may be inferred. This is frequently the case in assessing the extent of damages to health from coal utilization. Economic theory indicates that the control technology should be pushed to the point where the costs equal the benefits of residual removal. However, health benefits and costs have proved to be difficult to measure satisfactorily.

Statistical Problems

The data on coal characteristics are copious but still insufficient for many applications. First, the range in values reported is often large and presents statistical problems even for accessory elements such as iron, aluminum, and sulfur, which occur in substantial amounts in raw or clean coal; it is even more serious for the assessment of trace elements which occur within the parts per million or parts per billion range. Further, the variances in values are equally as important as the estimate of the means when variances are known to be large. Not only are large variances known to occur among seams for common coal characteristics, but they can also be large within seams and even within mines operating in a single seam. Those concerned with the economic recovery of elements or the environmental problems of disposal should not infer from published whole-coal averages that all mining basins or seams so described will produce the same proportions of these elements when subjected to various cleaning processes or degrees of weathering. Consequently, the economics of disposal or recovery will be affected by the occurrence or partitioning of elements in the different coal fractions (Gluskoter et al. 1977) as well as by the particle-size distribution of inorganic minerals so contained. In addition to the enriched mineral and chemical suite of elements (that is, those having a mean value higher than generally found in the earth's crust), coal contains a wide range of depleted trace elements. The organic affinity of these elements as described by the above authors can influence the costs of control because the efficacy of low-cost removal technologies (coal washing), as opposed to moderate-cost (stack-gas desulfurization) or high-cost technologies (conversion to gas or liquids), depends on such affinities. For example, the washability of such metals as arsenic, mercury, nickel or cadmium in Illinois coals, like the washability of sulfur, is partly a function of inorganic particle size and organic combination. In Illinois coal, these washabilities appear in the samples analyzed to be much greater than the washabilities of boron, beryllium or germanium. Therefore, coal chemistry and mineral engineering can have a significant bearing on the economics of recovery or disposal into the air from combustion. It is equally true that economic recovery or redistribution of elements into ground water, or their disposition as solid waste (Rose et al. 1976), will depend not only on coal characteristics but on the sequence of engineering applications.

Second, for trace elements, little attention has been given to the frequency distributions or characteristics for given coals. The same problem exists for small-sample bias in estimating means and variances even when the frequency distribution of the element is assumed to be well behaved, for example, normal or log-normal. Without designation of the distribution function, an efficient size sample for the estimation of recoverable tonnage by characteristic cannot be made. This is true of major seams for most statistical evaluations of trace-element amounts in raw coals. It is especially true for statistical analysis of clean-coal characteristics and washabilities even for major seams. Thus, small-sample bias causes a problem for the existing geological studies of accessory elements in coals, and it can invalidate many economic implications of costs or environmental damage based on such data.

Third, the statistical problem is also serious if special circumstances of coal deposition result in large variations of coal characteristics in areas of economic mining size. The genesis of an element leads to the conclusion that distinctly different means and variances characterize some mine sites. For example, the coal from mines in the Pittsburgh coal bed has a relatively high (4.5 percent) sulfur content. Other mines produce metallurgical-quality coal with much lower mean sulfur and ash content. This has given rise to large differences in washability data on the Pittsburgh coal seam. This problem has not been addressed by either economists or policymakers. Thus, even where relatively large amounts of an element occur, only a small part of the coal, as implied by chemical analysis, would yield anything like the total "estimate" for that element. It is likely that the amounts of trace elements reported in many cases will not be indicative of the total quantity of an element in stack emissions or as recoverable material in waste.

In the section following, estimates are made of the economic implications, notwithstanding the caveats given above.

Accessory Element Control and Reclamation

The economics of recovering an accessory element from coal depends on the amount of that element in the raw coal, how the element is concentrated by current coal-cleaning techniques or concentrated in the fly ash or bottom ash after coal burning, and on the cost of processing coal-waste material. The basis for economic recovery is the availability of very large quantities of waste from coal utilization.

At present, less than half the coal burned by utilities is cleaned, and most of this only to a moderate level. Almost all metallurgical coals are cleaned. The available data are strongly weighted by observations on the seams and wastes of southern Appalachia. The potential for reduction of accessory elements in coal cannot be forecast except by empirical tests or by statistical inference from the few published washability tests. There have been attempts to estimate the constituents of waste in gob piles or in fly ash from the burning of bituminous coal. The following is a summary of problems in the analysis of potential costs and savings from beneficiation:

1. Except for sulfur, published data are insufficient to enable quantification of the relation between raw-coal and clean-coal analyses for the entire United States. Many existing studies do not distinguish

among the levels of cleaning, and costs vary substantially with increasing levels of cleaning.

2. Washability characteristics for most accessory elements do not exist for specified size ranges and often are not complete enough to project the potentials of run-of-mine coal.

3. Because raw coals are quite variable, no standard flowsheet for coal-cleaning plants can be developed.

4. There is no way to compare cost savings for the preparation of coals of different washabilities except on a point estimate basis. Thus, generalizations cannot be made.

5. Preliminary studies give very little information about the cost of waste and refuse handling for specific coals.

6. Little published information is available on the cost of disposal of fine coal particles.

Nevertheless, a case can be made for the hypothesis that washing most coals to some level prior to combustion would save enough to compensate for the cost of cleaning.

Analyses of randomly selected increments of refuse obtained from coal-waste banks in the Monongahela River drainage basin show a wide variation in composition. Moisture ranges from 2 to 25 percent, volatile matter from 10 to 26 percent, fixed carbon from 7 to 41 percent, ash from 28 to 70 percent, sulfur from .3 to 7 percent and Btu content from 1,600 to 8,800 per pound. Typical chemical properties of fly ashes from bituminous coals, lignite, and limestone- and dolomite-modified fly ashes have received some study. The ranges in composition are as wide as in waste banks. However, it is clear that silicon dioxide (SiO_2) will dominate, constituting perhaps half of bituminous ashes, and the aluminum and iron oxides (Al_2O_3, Fe_2O_3) make up together perhaps one-third. Other trace elements appear too small and variable to predict a commercial future for the coals analyzed on the basis of present information. Studies by the Coal Research Bureau of West Virginia University showed several constituents in a typical fly ash (Table 1.34). The costs of bringing waste to this stage range from $1.00 per ton to $5.00 per ton or from 4.5¢ to 15¢ per MBtu in Appalachian coals exclusive of losses of carbon or adjustment to a clean-coal basis.

This leaves the question of economic evaluation of the production of alumina from fly ash. Using an evaluation by Katell (1977), who contemplated the Tatabanya process for a combined plant with annual production of 80,000 tons of high-grade alumina and 616,000 tons of quality cement, today's cost might reflect as much as $140 per ton for the alumina product and $33 per ton for the cement. This may not, however, be an optimal configuration for a plant because the clays surrounding the coals would often remain a better ore in conventional plants. Finally, the location of facilities, electricity sources, and access to both markets and factories would play a role in commercial ventures. Not all residuals from the many coal-burning locations are available for refining, and it may not pay to ship such material to central plants, even if the alternative ores were unavailable or less economic.

Because the economics of environmental control in mining and utilization have not been exhaustively surveyed, it should be noted that

TABLE 1.34 Typical Chemical and Physical Properties of Bituminous, Lignite, and Limestone- and Dolomite-Modified Fly Ashes

Chemical Properties (percent)	Bituminous	Limestone-modified*	Dolomite-modified*	Lignite
SiO_2	49.10	30.85	30.81	32.60
Al_2O_3	16.25	13.70	12.54	10.70
Fe_2O_3	22.31	11.59	10.72	10.00
TiO_2	1.09	0.68	0.42	0.56
CaO	4.48	33.58	17.90	18.00
MgO	1.00	1.49	14.77	7.31
Na_2O	0.05	1.12	0.72	0.87
K_2O	1.42	0.71	0.99	0.68
SO_3	0.73	2.20	8.09	2.60
C	2.21	1.12	1.76	0.11
Loss on ignition	2.55	1.03	1.95	0.62
H_2O soluble	2.51	22.11	20.39	8.55

* Coal ash constituent analysis for this limestone-modified fly ash is the same as that given for the bitiuminous fly ash.

SOURCE: Modified from Cockrell and Leonard (1970).

for many U.S. coals it is not yet possible to predict whether they can meet present standards required of new sources in power generation. If coal cleaning and stack-gas scrubbing can be applied sequentially, the apparent cost of clean-coal utilization in much of the United States remains below the cost of new oil or gas. Thus, it is apparent that coal will replace fuel oil and gas for use in large-scale boilers, and a great amount of waste will be generated. While these wastes will constitute potential resources as well as problems for the future, economic recovery of accessory elements in most cases is either questionable or impossible to predict at this point.

Finally, the matter of calculating the costs to human health or the environment of massive coal utilization are also under study elsewhere. The committee has not investigated the epidemiological effects of increased coal utilization, but, here, the economics of control look far more favorable than for the economic recovery of accessory elements. The data available suggest that a substantial portion of the accessory minerals enriched in coal seams can be significantly reduced by conventional coal-preparation or coal-waste treatment. Certainly, this appears true of mineral-matter-related elements, even those indigenous to the coal seams, unless they are of small particle size and homogeneously distributed throughout the seam. The exceptions, those accessory elements intimately bound to organic matter and easily volatilized, may pose problems of higher-cost capture that require research.

HEALTH EFFECTS

According to Piperno (1975), "no distinct causal relationships have been shown to exist between a pathological entity and coal-related trace element pollution; this of course does not mean there are none." Likewise, speaking of metals in the environment as a result of coal utilization, Vaughan et al. (1975) concluded that it was quite unlikely that any direct effects on health would result. These reports dealt at length with the potential dangers associated with coal utilization and the resulting redistribution of trace elements. Other reports, for example, Gough and Shacklette (1976), covered the more general field of elemental toxicities associated with natural and man-induced conditions. A wealth of information is given in reviews by Wilkes (1977) and Talmage (1977) on animal and human response to environmental pollutants.

It is not within the scope of this report to present a detailed review or analysis of these problems.[1]

Nevertheless, it is worth noting that information in this report concerning particulate emissions from coal combustion indicates that if a health problem does exist, new filter- and stack-gas scrubbing technologies may be on the verge of controlling it. Also, in the case of atmospheric emissions from proposed coal-conversion processes, it appears very likely that many potential pollutants can be contained. However, the nature of health hazards to employees working within such a plant is unclear.

The disposal of solid wastes resulting from the increased use of coal will probably cause the greatest health hazards because of the chances for ground- and surface-water pollution, unless new research leads to better controls. Moreover, the problems of controlling many of the wastes will be new and will be different from those being encountered today.

While avoiding a comprehensive review, there are several health-related points that should be considered. First, it has been determined, for example, that forage plants growing on western coal-mine spoils may contain sufficient quantities of trace elements to cause metabolic imbalances in cattle or sheep (Erdman and Evans 1976a,b). This seemed to be the case for Mo in sweet clover. Concentrations of Cd, Co, F, U, and Zn ranged from 140 to 400 percent higher in wheat grass grown on coal-mine spoils than in those grown on control areas. If additional large areas of western coals are strip-mined, means for assessing potential health hazards need to be developed.

Second, it has been reported that rock formations (shales) encountered in some underground coal mining in northeastern Pennsylvania contain appreciable amounts of Ni, Co, Cr, Mn, and Fe (El-Ashry 1971, and El-Ashry and Getzoff 1974). The pattern of relative concentrations of these elements was found to correlate with the distribution of lung cancer among coal miners who worked in these mines. The study thus suggested that the incidence of lung cancer in these miners was related to prolonged exposure to rock dust containing high concentrations of these and perhaps other elements.

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[1] A detailed study of the trace-element geochemistry of coal resource development related to health is currently under way by the Academy's Panel on Trace-Element Geochemistry of Coal Resource Development Related to Health, Subcommittee on the Geochemical Environment in Relation to Health and Disease, U.S. National Committee for Geochemistry.

Finally, it should not be assumed that accessory elements in coal are always hazardous. Many trace elements are much maligned even though essential to life. A case in point is selenium, one of the few elements now known to be enriched in coal and sufficiently volatile to cause concern. Schrauzer (1977) stated that the view that selenium is a highly toxic carcinogen is based on erroneous concepts. Although admittedly toxic to rodents at 5 parts per million (relatively, a very high concentration) in drinking water, selenium in small amounts is in reality an essential trace element and is one of the few anticarcinogenic elements known. Research should be designed to show the positive as well as the negative health aspects of accessory element redistribution.

RECOMMENDATIONS FOR RESEARCH

1. Renew efforts to determine the fundamental physical structure of coal.
2. Determine relationships, if any, of surrounding rocks to accessory element composition of coal.
3. Determine the organically associated elements, their relative abundances, and classes of compounds in coal.
4. Study the distribution of accessory elements in different coal macerals.
5. Develop geographic and stratigraphic maps of accessory element concentrations for U.S. coals. Additional compositional data and thorough evaluation of currently available data are needed.
6. Intensify efforts to interpret variations of accessory elements in U.S. coals in terms of associated geologic features.
7. Conduct research on both old and new methods of coal cleaning and evaluate effects on accessory element removal.
8. Determine the interrelationships for composition of whole coal, the cleaning processes used, and the composition of the resulting waste material.
9. Develop new methods for the recovery of accessory elements from coal refuse.
10. Evaluate new coal-preparation methods with regard to accessory element composition, and the physical properties and solubilities of the solid wastes produced.
11. For the western United States, conduct additional studies of the effects of coal-fired power plants and reclamation of strip mines on the relatively pristine environment. Also study the long-term health effects, if any, on vegetation, animals, and humans.
12. Conduct tests and research on new stack-gas emission controls, being certain to include fabric baghouse filtration as an integral part of the studies.

13. Investigate hazards associated with disposal of coal wastes, especially those containing soluble forms of accessory elements, in underground and strip mines under different environmental conditions. Fluidized-bed combustion wastes should be given priority.
14. Make plans to study the composition and disposition of wastes, effluents and emissions from the first commercial U.S. coal-conversion plants. Baseline studies should begin now so that the fate of accessory elements within and surrounding the plants can eventually be determined accurately.
15. Study the effects of underground gasification on the redistribution of accessory elements in ground water and product gas.
16. Relate the accessory elements in products, byproducts, and wastes from coal-conversion processes to the composition of the wholecoal feed and to plant operating variables.
17. Develop predictive, laboratory hazard-tests that take into account the solubility, mobility, and toxicity of accessory elements in coal wastes.
18. Determine the most effective treatment for trace-element removal from various types of waste water, such as mine and coal-pile drainage, coal-conversion process water, leachates from solid wastes, and ash-pond sluice water.
19. Determine the effectiveness of different earth materials and other types of liners for prevention of ground- and surface-water pollution by leachates from coal wastes.
20. Determine the mechanisms and materials by which highly mobile elements derived from coal wastes and effluents may be attenuated.

APPENDIX A--SUPPLEMENTAL DATA TABLES

TABLE A1.1 Arithmetic Mean, Observed Range, Geometric Mean, and Geometric Deviation of 36 Elements in 53 Pennsylvania Anthracite Region Samples (whole-coal basis). (For comparison, average shale values are listed)

Element	Arithmetic Mean (abundance)	Observed Range		Geometric Mean (expected value)	Geometric Deviation	Average Shale
		Minimum	Maximum			
Percent						
Si	2.7	3.6	9.4	2.2	2.0	27.3
Al	2.0	.46	6.4	1.8	1.7	8.0
Ca	.072	.007	1.3	.045	2.6	2.21
Mg	.055	.015	.239	.044	2.0	1.55
Na	.046	.005	.287	.033	2.3	.96
K	.24	.019	1.5	.16	2.4	2.66
Fe	.44	.055	4.1	.29	2.4	4.72
Ti	.15	.014	.53	.12	1.9	.46
Parts per million (ppm)						
Mn	18	4.8 L	210	4.2	6.2	850
As	6	.7	140	4	2.7	13
Cd	.26	.02	1.37	.19	2.3	.3
Cu	27.3	5.9	274	21.5	2.0	45
F	61	20 L	290	41	2.4	740
Hg	.15	.03	1.25	.11	2.2	.4
Li	33.1	4.0	162	24.1	2.2	66
Pb	9.6	1.0	24.2	7.5	2.0	20
Sb	.9	.1 L	12.5	.6	2.6	1.5
Se	3.5	.6	13	2.7	2.0	.6
Th	5.4	2.8	14.4	4.7	1.8	12
U	1.5	.3	25.2	1.2	1.9	3.7
Zn	16.1	.1	64.6	10.0	2.7	95
B	10	2	20	10	1.8	100
Ba	100	10	300	70	2.0	580
Be	1.5	.2	5	1	1.9	3.0
Co	7	.3 L	50	5	2.2	19
Cr	20	5	70	20	1.7	90
Ga	7	1.5	20	5	1.8	19
Mo	2	.5	15	1.5	20	2.6
Nb	3	.5 L	15	3	1.8	11
Ni	20	3	70	15	1.8	68
Sc	5	.7	20	3	1.8	13
Sr	100	5	700	50	3.1	300
V	20	2	70	20	1.9	130
Y	10	1	30	7	1.7	26
Yb	1	.15	3	.7	1.7	2.6
Zr	50	7	50	30	1.9	160

Note: As, F, Hg, Sb, Se, Th, and U values used to calculate the statistics were determined directly on whole coal. All other values used were calculated from determinations made on coal ash. L means less than the value shown.

SOURCE: Turekian and Wedepohl (1961) (shale); Swanson et al. (1976) (anthracite).

TABLE A1.2 Arithmetic Mean, Observed Range, Geometric Mean, and Geometric Deviation of 36 Elements in 331 Appalachian Region Coal Samples (whole-coal basis). (For comparison, average shale values are listed)

Element	Arithmetic Mean (abundance)	Observed Range		Geometric Mean (expected value)	Geometric Deviation	Average Shale
		Minimum	Maximum			
Percent						
Si	2.7	0.22	25.0	1.2	2.2	27.3
Al	1.6	.19	10.5	1.3	2.0	8.0
Ca	.12	.023L	2.0	.093	2.0	2.21
Mg	.068	.007	1.10	.052	2.0	1.55
Na	.032	.025	.242	.025	2.0	.96
K	.23	.008	2.4	.13	2.8	2.66
Fe	1.9	.059	9.3	1.0	3.0	4.72
Ti	.09	.011	.49	.074	2.1	.46
Parts per million (ppm)						
Mn	620	3.9 L	1,000	200	4.6	850
As	27	.5	357	11	3.8	13
Cd	.7	.03 L	6.8	.3	3.6	.3
Cu	24	1.2	911	16.0	2.4	45
F	80	20 L	586	60	2.1	740
Hg	.24	.01	3.30	.14	2.7	.4
Li	27.6	1.8	150	18.8	2.4	66
Pb	15.3	1	69.9	10.9	2.3	20
Sb	1.2	.1	34.6	.8	2.4	1.5
Se	4.7	.1 L	150	3.5	2.2	.6
Th	4.9	2.2	47.8	2.8	2.8	12
U	1.4	.2 L	10.5	1.0	2.3	3.7
Zn	20.0	1.5	1,072	12.8	2.6	95
B	30	1	100 G	20	3.0	100
Ba	100	7	700	70	3.2	580
Be	2	.3	7	2	1.9	3
Co	7	.5	300 G	5	2.2	19
Cr	20	.5 L	70	15	2.2	90
Ga	7	.7	30	7	2.0	19
Mo	3	.2 L	30	2	2.6	2.6
Nb	5	.2	20	3	2.3	11
Ni	15	1.5	300 G	15	2.1	68
Sc	5	.7	15	3	2.0	13
Sr	100	7	700 G	70	2.3	300
V	20	2	150	20	2.0	130
Y	10	2	70	7	1.8	26
Yb	1	.15	5	.7	1.8	2.6
Zr	50	2	300	30	2.8	160

Note: As, F, Hg, Sb, Se, Th, and U values used to calculate the statistics were determined directly on whole coal. All other values used were calculated from determinations made on coal ash. L means less than the values shown, and G means greater than the value shown.

SOURCE: Turekian and Wedepohl (1961) (shale); Swanson et al. (1976) (anthracite).

TABLE A1.3 Arithmetic Mean, Observed Range, Geometric Mean, and Geometric Deviation of 36 Elements in 155 Interior Province Coal Samples (whole-coal basis). (For comparison, average shale values are listed)

Element	Arithmetic Mean (abundance)	Observed Range		Geometric Mean (expected value)	Geometric Deviation	Average Shale
		Minimum	Maximum			
Percent						
Si	2.0	.14	9.0	1.4	2.3	27.3
Al	.97	.15	3.6	.77	2.0	8.0
Ca	1.2	.025	6.3	.50	3.8	2.21
Mg	.089	.009	1.0	.063	2.3	1.55
Na	.035	.002	.21	.026	2.2	.96
K	.16	.011	.53	.11	2.4	2.66
Fe	3.3	.23	16	2.3	2.4	4.72
Ti	.052	.01	.21	.040	2.1	.46
Parts per million (ppm)						
Mn	138	4.4	4,400	72	3.1	850
As	21	1 L	240	12	2.9	13
Cd	7.1	.02 L	100	.12	18.3	.3
Cu	20.2	3.7	158	16.3	1.9	45
F	71	20 L	330	58	1.9	740
Hg	.14	.01 L	.83	.10	2.3	.4
Li	11	.44	80	7.0	2.7	66
Pb	55	.7 L	283	19	4.3	20
Sb	1.7	.1 L	16	.8	3.4	1.5
Se	4.6	.23	75	2.8	2.7	.6
Th	5.2	3.0 L	79	1.6	4.8	12
U	3.3	.2 L	43	1.4	3.8	3.7
Zn	373	1.2	18,000	58	6.9	95
B	100	1.5 L	200	50	3.4	100
Ba	70	5	3,000	30	2.6	580
Be	3	.1 L	5	1.5	3.1	3
Co	7	1	100	7	2.3	19
Cr	15	2	70	10	2.0	90
Ga	5	.5 L	10	3	2.0	19
Mo	5	.7 L	50	2	2.8	2.6
Nb	1.5	.5 L	7	.7	2.6	11
Ni	30	1	200	18	2.4	68
Sc	3	.51	15	3	2.1	13
Sr	50	3	5,000 G	30	2.8	300
V	20	3	150	20	2.1	130
Y	10	1.5 L	70	7	1.9	26
Yb	.7	.2	3	.7	2.0	2.6
Zr	15	2	70	10	2.0	160

Note: As, F, Hg, Sb, Se, Th, and U values used to calculate the statistics were determined directly on whole coal. All other values used were calculated from determinations made on coal ash. L means less than the value shown, and G means greater than the value shown.

SOURCE: Turekian and Wedepohl (1961) (shale); Swanson et al. (1976) (anthracite).

TABLE A1.4 Average Zinc and Cadmium Concentrations in Whole Coal Samples from Southeastern Iowa, Missouri and Southeastern Kansas (summarized by County)

State	County	Thickness Category or Bed Name	No. of Samples	Whole Coal	
				Cd ppm	Zn ppm
Southeastern Iowa - northeastern Missouri					
Iowa	Mahaska	≥0.46 m	9	0.8	403
Iowa	Lucas	≥0.46 m	2	.2L	106
Iowa	Monroe	≥0.46 m	4	.2	168
Iowa	Wapello	≥0.46 m	18	7.7	1,180
		<0.46 m	21	8.1	1,590
Iowa	Appanoose	≥0.46 m	1	.7	38
		<0.46 m	8	15.6	1,180
Iowa	Davis	≥0.46 m	2	2.7	472
		<0.46 m	3	.7L	85
Missouri	Putnam	Lexington	22	18.1	1,600
Missouri	Sullivan	—do—	1	4.0	174
North-central Missouri					
Missouri	Macon	Mulky	4	0.2	17.1
		Bevier-Wheeler	6	1.0	125
Missouri	Randolph	—do—	12	.5	67
Missouri	Howard	—do—	5	43.5	4,700
Southwestern Missouri - southeastern Kansas					
Missouri	Henry	Mulky	2	0.1L	17.5
		Croweburg	4	12.1	1,080
		Fleming	2	1.2	283
		Tebo	6	12.4	1,567
		Wier-Pittsburgh	3	.2L	17.7
Missouri	St. Clair	Riverton (?)	1	.2L	18.2
Missouri	Bates	Mulberry	4	60.2	5,060
Missouri	Vernon	Croweburg	4	.2L	40.5
		Fleming	4	14.3	2,700
		Mineral	2	12.3	1,990
Missouri	Barton	Drywood	4	.2L	16.0
		Rowe	4	.2L	19.0
Kansas	Crawford	Croweburg	3	.2L	33.4
		Mineral	2	.1L	42.6
		Dry Wood	3	58.3	18,800
		Rowe	6	.2L	46.6
Kansas	Cherokee	—do—	2	.2L	14.4

Note: L after a value means less than the value shown. Missouri and Kansas coal analyses are summarized by bed. Since correlations of coal beds between core holes in Iowa are lacking, Zn and Cd concentrations are summarized in two thickness categories, beds ≥0.46 meters (15 inches) and beds <0.46 meters thick.

SOURCE: Hatch et al. (1976a).

TABLE A1.5 Summary of Trace Element Analysis of Illinois Basin Coal

Element	Mean Values (ppm) Moisture-free Whole Coal Illinois Basin (114 samples)
Ag	0.03
As	14
B	113
Ba	100
Be	1.7
Br	13
Cd	1.5
Ce	14
Co	7.1
Cr	18
Cs	1.4
Cu	15
Dy	1.1
Eu	0.26
F	66
Ga	3.2
Ge	6.9
Hf	0.54
Hg	0.20
I	1.6
In	0.16
La	6.8
Lu	0.09
Mn	53
Mo	8.0
Ni	21
P	64
Pb	31
Rb	19
Sb	1.2
Sc	2.7
Se	2.2
Sm	1.2
Sn	3.2
Sr	35
Ta	0.15
Tb	0.22
Th	2.1
Tl	0.66
U	1.5
V	31
W	0.83
Yb	0.56
Zn	251
Zr	47

SOURCE: Ruch et al. (1974).

TABLE A1.6 Arithmetic Mean, Observed Range, Geometric Mean, and Geometric Deviation of 35 Elements in 34 Gulf Province Lignite Samples (whole-lignite basis). (For comparison, average shale values are listed)

Element	Arithmetic Mean (abundance)	Observed Range		Geometric Mean (expected value)	Geometric Deviation	Average Shale
		Minimum	Maximum			
Percent						
Si	6.6	0.57	17.9	4.2	2.5	27.3
Al	2.1	.34	.6	1.6	2.2	8.0
Ca	1.2	.02	2.4	.60	3.2	2.21
Mg	.291	.013	.528	.170	2.8	1.55
Na	.732	.003	.190	.009	3.3	.96
K	.30	.012	1.3	.15	3.3	2.66
Fe	2.2	.14	5.4	1.6	2.2	4.72
Ti	.16	.02	.75	.11	2.4	.46
Parts per million (ppm)						
Mn	240	7.4	690	51	3.7	850
As	6	1	16	5	2.0	13
Cd	1.3	.11 L	5.50	.2	3.0	.3
Cu	28	3.3	289	20.0	2.4	45
F	124	24	350	91	2.2	740
Hg	.18	.03	1.00	.13	2.2	.4
Li	28	.9	145	14.0	3.3	66
Pb	20	2.8 L	129	2.8	2.3	20
Sb	.9	.2	5.2	.7	2.2	1.5
Se	7.0	1.8	17	5.8	1.8	.6
Th	8.3	3.0 L	28.4	3.0	2.6	12
U	3.2	.5	16.7	2.4	2.1	3.7
Zn	40	5.4	201	28.0	2.3	95
B	100	10 L	200	100	1.6	100
Ba	200	15	700	150	2.1	580
Be	2	.2	15	2	2.5	3
Co	7	1	30	5	2.1	19
Cr	20	3	70	15	2.4	90
Ga	10	2	30	7	2.2	19
Mo	3	.5	10	.7	2.1	2.6
Nb	7	1	70	2	6.7	11
Ni	20	3	70	15	2.0	68
Sc	7	1	15	5	1.9	13
Sr	200	7	700	150	2.5	300
V	50	7	100	30	2.1	130
Y	20	2	50	15	2.2	26
Yb	2	.3	5	1.5	2.0	2.6
Zr	70	7	200	50	2.6	160

Note: As, F, Hg, Sb, Se, Th, and U values used to calculate the statistics were determined directly on whole-coal. All other values used were calculated from determinations made on coal ash. L means less than the value shown.

SOURCE: Turekian and Wedepohl (1961) (shale); Swanson et al. (1976) (anthracite).

TABLE A1.7 Arichmetic Mean, Observed Range, Geometric Mean, and Geometric Deviation of 36 Elements in 490 Northern Great Plains Province Coal Samples (whole-coal basis). (For comparison, average shale values are listed)

Element	Arithmetic Mean (abundance)	Observed Range		Geometric Mean (expected value)	Geometric Deviation	Average Shale
		Minimum	Maximum			
Percent						
Si	1.4	0.01 L	25	1.0	2.3	27.3
Al	.73	.11	11	.61	1.8	8.0
Ca	1.2	.086	7.8	1.0	1.6	2.21
Mg	.238	.013	.758	.218	1.5	1.55
Na	.122	.001	.672	.067	3.0	.96
K	.042	.001L	1.2	.018	3.7	2.66
Fe	.55	.010	14	.36	2.5	4.72
Ti	.040	.004	.13	.034	1.7	.46
Parts per million (ppm)						
Mn	50	90 L	440	33	2.5	850
As	4	1 L	45	2	2.5	13
Cd	.08	.02	2.7	.04	2.8	.3
Cu	10.5	.34	76	8.2	2.0	45
F	47	20 L	340	38	1.9	740
Hg	.11	.01 L	3.8	.08	2.2	.4
Li	5.6	.32 L	49.2	3.6	2.6	66
Pb	5.9	1.2 L	76	4.8	1.9	20
Sb	.6	.1 L	43	.4	2.6	1.5
Se	.9	.1 L	13	.6	2.4	.6
Th	4.3	.04	28	3.4	2.0	12
U	.9	.07	7.5	.6	2.6	3.7
Zn	17.9	1.0	218	9.4	3.1	95
B	70	15	300	70	1.8	100
Ba	500	10	2,000	300	2.3	580
Be	.7	.1 L	15	.5	2.4	3
Co	2	.3 L	20	2	2.1	19
Cr	5	.5	100	3	2.3	90
Ga	2	.5	20	2	1.9	19
Mo	2	.3 L	70	1.5	2.4	2.6
Nb	1.5	.7 L	30	.7	3.3	11
Ni	5	.5 L	300	2	2.5	68
Sc	2	.5 L	20	1.5	1.8	13
Sr	300	15	1,500	200	2.3	300
V	15	1	150	10	2.3	130
Y	5	.7 L	30	3	2.1	26
Yb	.3	.07 L	3	.3	2.0	2.6
Zr	15	2	150	15	1.8	160

Note: As, F, Hg, Sb, Se, Th, and U values used to calculate the statistics were determined directly on whole-coal. All other values used were calculated from determinations made on coal ash. L means less than the value shown.

SOURCE: Turekian and Wedepohl (1961) (shale); Hatch and Swanson (1977) (anthracite).

TABLE A1.8 Arithmetic Mean, Observed Range, Geometric Mean, and Geometric Deviation of 36 Elements in 295 Rocky Mountain Province Coal Samples (whole-coal basis). (For comparison, average shale values are listed)

Element	Arithmetic Mean (abundance)	Observed Range		Geometric Mean (expected value)	Geometric Deviation	Average Shale
		Minimum	Maximum			
Percent						
Si	3.2	0.9	23	2.3	2.3	27.3
Al	1.6	.14	13	1.1	2.3	8.0
Ca	.61	.05	3.7	.48	2.0	2.21
Mg	.107	.015	.76	.089	1.8	1.55
Na	.155	.002	.76	.055	4.2	.96
K	.092	.003	1.7	.041	3.6	2.66
Fe	.64	.10	4.2	.34	3.1	4.72
Ti	.062	.001L	.54	.047	2.1	.46
Parts per million (ppm)						
Mn	33	2.7	492	20	2.6	850
As	2	1 L	50	2	2.5	13
Cd	.08	.021	.50	.05	2.7	.3
Cu	10.8	1.3	100	8.4	2.0	45
F	95	20 L	920	69	2.2	740
Hg	.08	.01	1.48	.05	2.4	.4
Li	13	.44 L	82.9	8.0	2.7	66
Pb	6.5	.95	62	4.7	2.2	20
Sb	.4	.05 L	5.2	.3	2.2	1.5
Se	1.6	.10 L	5.7	1.2	2.1	.6
Th	4.2	1.7	34.8	2.9	2.5	12
U	1.9	.1	23.8	1.1	2.8	3.7
Zn	10.7	1.0	380	6.8	2.6	95
B	70	7	300	70	2.2	100
Ba	300	3	1,500	150	2.6	580
Be	.7	.05	3	.5	2.3	3
Co	2	.3	10	1.5	2.0	19
Cr	5	.5	70	5	2.2	90
Ga	5	.3	30	3	2.3	19
Mo	2	.2	15	1.5	2.3	2.6
Nb	1	.3	30	.5	2.6	11
Ni	3	.7	20	2	2.1	68
Sc	2	.3	15	1.5	2.0	13
Sr	100	5	700	100	2.1	300
V	15	1.5	100	100	2.1	130
Y	7	.5	30	5	2.1	26
Yb	.7	.03	3	.5	2.2	2.6
Zr	30	3	100	20	2.3	160

Note: As, F, Hg, Sb, Se, Th, and U values used to calculate the statistics were determined directly on whole-coal. All other values used were calculated from determinations made on coal ash. L means less than the value shown.

SOURCE: Turekian and Wedepohl (1961) (shale); Hatch and Swanson (1977) (anthracite).

TABLE A1.9 Arithmetic Mean, Observed Range, Geometric Mean, and Geometric Deviation of 36 Elements in 18 Alaska Coal Samples (whole-coal basis). (For comparison, average shale values are listed)

Element	Arithmetic Mean (abundance)	Observed Range		Geometirc Mean (expected value)	Geometric Deviation	Average Shale
		Minimum	Maximum			
Percent						
Si	2.9	0.53	10.4	2.2	2.1	27.3
Al	1.5	.48	4.6	1.2	1.8	8.0
Ca	1.0	.12	1.8	.79	2.1	2.21
Mg	2.5	.057	.43	.21	1.7	1.55
Na	.018	.007L	.079	.012	2.3	.96
K	.12	.016	.87	.076	2.5	2.66
Fe	.38	.12	1.2	.30	2.0	4.72
Ti	.077	.022	.23	.065	1.8	.46
Parts per million (ppm)						
Mn	61	16L	132	31	3.3	850
As	3	1	5	3	1.6	13
Cd	.2L	.1L	.7	.2L	2.3	.3
Cu	16.8	8.2	48.8	5.1	1.6	45
F	90	30	335	14	1.9	740
Hg	4.4	.02	63	.21	14	.4
Li	10.1	1.3	43	6.7	2.5	66
Pb	5.9	2.0	15	5.3	1.6	20
Sb	2.7	.5	8.2	1.8	2.4	1.5
Se	2.0	.2L	11	.9	3.6	.6
Th	4.4	3.0L	18	3.1	2.4	12
U	1.2	.4	5.2	1.0	1.9	3.7
Zn	24	2.3	435	9.6	4.0	95
B	70	15	200	70	2.0	100
Ba	700	20	1,500	300	3.0	580
Be	.7	.2	3	.3	3.6	3
Co	5	1	30	3	2.4	19
Cr	15	5	70	15	1.9	90
Ga	5	2	10	3	1.8	19
Mo	1.5	1	2	1.5	1.4	2.6
Nb	3	1.5L	7	2	1.8	11
Ni	10	2	30	10	1.9	68
Sc	5	1.5	15	5	1.9	13
Sr	100	50	200	100	1.6	300
V	30	15	100	30	1.7	130
Y	10	3	50	7	2.3	26
Yb	1	.3	3	.7	2.2	2.6
Zr	20	10	70	20	1.7	160

Note: As, F, Hg, Sb, Se, Th, and U values used to calculate the statistics were determined directly on whole coal. All other values used were calculated from determinations made on coal ash. L means less than value shown.

SOURCE: Turekian and Wedepohl (1961) (shale); Swanson et al. (1976) (anthracite).

TABLE A1.10 Elemental Content (ppm) of Floor Rock Samples from Eastern Interior Province. Given are Minimum and Maximum as well as Geometric Mean (GM) and Geometric Deviation (GD)

Element	Minimum	Eastern Interior (29)		(GD)	Average U.S. Coal	Average Shale
		Maximum	GM			
Ag	.16	.44	.22	(1.4)	—	—
As	1.7	89.	7.7	(2.5)	15.	13.
B	65.	260.	128.	(1.4)	50.	100.
Ba	180.	2,000.	569.	(1.7)	150.	580.
Be	3.	15.	6.	(1.4)	2.	3.
Cd	.1	5.3	.27	(2.6)	1.3	.3
Co	8.	120.	20.	(1.7)	7.	19.
Cr	60.	180.	105.	(1.3)	15.	90.
Cu	23.	90.	40.	(1.4)	19.	45.
F	170.	2,500.	530.	(1.8)	74.	740.
Ga	18.	40.	29.	(1.2)	7.	19.
Ge	5.	11.	7.	(1.3)	—	—
Hg	.01	2.0	.05	(3.3)	.18	.4
La	30.	240.	70.	(1.6)	—	—
Li	36.	380.	91.	(2.0)	20.	66.
Mn	53.	520.	164.	(1.9)	100.	850.
Mo	2.	24.	4.	(1.5)	3.	2.6
Ni	36.	210.	71.	(1.5)	15.	68.
Pb	12.	510.	39.	(2.4)	16.	20.
Sb	.47	25.7	1.1	(2.3)	1.1	1.5
Se	.1	7.5	1.4	(3.0)	4.1	.6
Sn	7.	16.	11.	(1.3)	—	—
Sr	43.	2,200.	190.	(2.3)	100.	300.
Th	8.	22.	15.	(1.3)	4.7	12.0
U	2.8	9.2	4.4	(1.3)	1.8	3.7
V	66.	310.	142.	(1.4)	100.	300.
Y	10.	95.	35.	(1.6)	10.	26.
Yb	.3	10.	5.	(1.8)	1.	2.6
Zn	27.	210.	88.	(1.8)	39.	95.
Zr	50.	710.	250.	(1.7)	30.	160.

SOURCE: Medlin (1977).

TABLE A1.11 Elemental Concentration (ppm) of Coal Partings from Appalachian Basin and Eastern Interior Provinces. Minimum and Maximum Values are Given as well as Geometric Mean (GM) and Geometric Deviation (GD)

Element	Appalachian (31)				Eastern Interior (18)				Average U.S. Coal (799)	Average Shale
	Minimum	Maximum	GM	(GD)	Minimum	Maximum	GM	(GD)		
Ag	.10	.46	.18	(.18)	.17	6.2	.55	(3.2)	—	—
As		15.7 (17)	7.3	(2.0)	.94	949.	19.4	(3.9)	15.0	13.
B	46.	200.	100.	(1.3)		2,400.	312.	(2.4)	50.	100.
Ba	290.	2,190.	538.	(1.6)	33.	900.	352.	(2.0)	150.	580.
Be	1.8	11.8	4.3	(1.5)	3.	130.	10.7	(3.0)	2.	3.0
Cd	.10	.63	.17	(1.8)	.11	28.	1.0	(5.4)	1.3	.3
Co	3.	26.	10.	(1.8)	12.	240.	32.	(2.3)	7.	19.
Cr	52.	154.	98.	(1.3)	20.	890.	100.	(2.3)	15.	90.
Cu	16.	190.	53.	(1.6)	21.	330.	74.	(1.9)	19.	45.
F	200.	1,100.	407.	(1.5)	20.	2,300.	280.	(3.6)	74.	740.
Ga	19.	63.	33.	(1.3)	16.	140.	34.	(1.9)	7.	19.
Ge	3.	8.	4.4	(1.2)	5.	1,100.	23.	(5.3)	—	—
Hg	.01	.40	.06	(2.5)	.09	2.4	.19	(2.2)	.18	.4
La	15.	110.	40.	(1.6)	24.	180.	58.	(1.7)	—	—
Li	26.	310.	120.	(1.8)	11.	490.	79.	(3.3)	20.	66.
Mn	29.	1,200.	142.	(2.2)	36.	2,100.	353.	(2.5)	100.	850.
Mo	2.	5.	2.4	(1.2)	3.8	230.	21.6	(4.0)	3.	2.6
Ni	7.	79.	33.	(1.7)	55.	1,500.	134.	(2.5)	15.	68.
Pb	12.	51.	26.	(1.5)	11.	4,300.	83.	(5.4)	16.	20.
Sb		1.33 (17)	.89	(1.4)	.22	7.1	1.5	(2.5)	1.1	1.5
Se		26.8 (25)	5.3	(2.0)	1.1	53.7	6.4	(2.7)	4.1	.6
Sn	7.	15.	9.	(1.4)	7.	50.	12.	(1.6)	—	—
Sr	70.	1,100.	151.	(1.9)	18.	1,500.	211.	(2.8)	100.	300.
Th		22. (19)	16.	(1.2)		(12) 25.	12.	(1.8)	4.7	12.
U		7. (19)	4.5	(1.2)		(17) 79.	4.7	(2.8)	1.8	3.7
V	60.	180.	119.	(1.3)	15.	1,100.	127.	(2.6)	20.	130.
Y	12.	47.	26.	(1.4)	4.	310.	37.	(3.3)	10.	26.
Yb	3.	9.	5.	(1.2)	.2	17.	5.	(2.6)	1.	2.6
Zn	.32	190.	56.	(3.0)	14.	5,200.	106.	(5.2)	39.	95.
Zr	85.	1,500.	168.	(1.7)	12.	2,600.	210.	(3.0)	30.	160.

SOURCE: Medlin (1977).

TABLE A1.12 Elemental Concentration (ppm) of Roof Rock from Interior and Gulf Coast Provinces. Given are Minimum and Maximum Values as well as Geometric Mean (GM) and Geometric Deviation (GD) for Eastern Interior and Minimum and Maximum Values and Arithmetic Mean for Gulf Coast Samples

Element	Eastern Interior (28)				Gulf Coast (3)			Average U.S. Coal (699)	Average Shale
	Minimum	Maximum	GM	(GD)	Minimum	Maximum	Arithmetic Mean (3 Samples)		
Ag	.19	7.4	1.1	(4.1)	.19L	.48	.3	—	—
As	3.7	49.8	12.1	(2.1)	3.	8.	5.	15.	13.
B	5.	240.	108.	(2.2)	48.	79.	67.	50.	100.
Ba	18.	1,600.	441.	(2.3)	670.	750.	690.	150.	580.
Be	1.5	13.	4.5	(1.8)	1.4	5.0	3.	2.	3.
Cd	.11	140.	1.2	(11.)	.10	.42	.28	1.3	.3
Co	4.	46.	18.	(1.9)	9.	21.	17.	7.	19.
Cr	18.	930.	119.	(2.5)	61.	82.	74.	15.	90.
Cu	12.	180.	46.	(2.2)	13.	36.	27.	19.	45.
F	100.	3,200.	598.	(2.4)	220.	620.	443.	74.	740.
Ga	6.	62.	28.	(1.7)	8.	27.	18.	7.	19.
Ge	5.	11.	7.6	(1.4)	9. L	—	9. L	—	—
Hg	.01	1.2	.09	(3.8)	.06	.07	.03	.18	.4
La	17.	360.	62.	(1.8)	35.	49.	53.	—	—
Li	10.	140.	45.	(1.7)	22.	58.	44.	20.	66.
Mn	35.	3,500.	529.	(2.8)	85.	170.	138.	100.	850.
Mo	5.	980.	40.	(5.1)	4. L		4. L	3.	2.6
Ni	9.	790.	70.	(2.6)	25.	120.	63.	15.	68.
Pb	11.	120.	21.	(1.7)	10. L	14.	11.	16.	20.
Sb	.3	7.6	1.0	(2.5)	.7	.9	.8	1.1	1.5
Se	.01	70.	(25)* 2.1	(8.9)	.2	2.2	1.3	4.1	.6
Sn	15.	20.	17.	(1.1)	13. L		13. L	—	—
Sr	16.	3,100.	180.	(2.5)	110.	130.	120.	100.	300.
Th	9.	41.	(22)* 15.	(1.4)	9.	13.	10.	4.7	12.0
U	3.0	289.	(26)* 8.9	(3.5)	2.9	4.2	3.6	1.8	3.7
V	7.	1,900.	143.	(3.0)	50.	230.	150.	100.	300.
Y	4.	380.	33.	(2.2)	—	—	37.	10.	26.
Yb	.9	31.	(26)* 5.	(1.8)	2.	3.	5.0	1.	2.6
Zn	15.	4,600.	117.	(3.6)	70.	220.	133.	39.	95.
Zr	33.	860.	192.	(2.0)	190.	460.	307.	30.	160.

Note: * indicates number of samples. L means less than value shown.

SOURCE: Medlin (1977).

TABLE A1.13 Elemental Concentration (Geometric Mean, ppm) of Floor Rock from Gulf Coast and Eastern Interior Provinces; Coal Partings from Appalachian Basin and Eastern Interior Provinces; and Roof Rock from Gulf Coast and Eastern Interior Provinces. (For comparison, elemental content of U.S. coal [whole-coal basis] and average shale [Turekin and Wedepohl, 1961] are also given)

Element	Floor Rock		Partings		Roof Rock		Average U.S. Coal	Average Shale
	Gulf Coast	Eastern Interior	Appalachian Basin	Eastern Interior	Eastern Interior	Gulf Coast		
Ag	.2	.2	.2	.7	1.1	.3	—	—
As	3.	7.7	6.4	23.1	12.1	5.	15.	13.
B	80.	128.	100.	275.	108.	67.	50.	100.
Ba	635.	569.	534.	352.	441.	690.	150.	580.
Be	3.	6.	4.	11.	4.	3.	2.	3.
Cd	.33	.36	.23	1.0	1.2	.28	1.3	.3
Co	8.	20.	10.	32.	18.	17.	7.	19.
Cr	87.	105.	98.	100.	119.	74.	15.	90.
Cu	28.	40.	53.	74.	46.	27.	19.	45.
F	565.	530.	407.	327.	598.	443.	74.	740.
Ga	25.	29.	33.	34.	28.	18.	7.	19.
Ge	5. L	7.	4. L	88.	8. L	9. L	—	—
Hg	.05	.05	.06	.19	.09	.03	.18	.4
La	38.	70.	42.	65.	62.	53.	—	—
Li	49.	91.	119.	79.	45.	44.	20.	66.
Mn	220.	164.	142.	353.	529.	138.	100.	850.
Mo	4. L	6.	3.1	26.	40.	4. L	3.	2.6
Ni	34.	71.	33.	134.	70.	63.	15.	68.
Pb	10.	39.	26.	83.	21.	11.	16.	20.
Sb	.9	1.1	.9	1.7	1.0	.8	1.1	1.5
Se	2.0	1.3	5.1	6.4	2.1	1.3	4.1	.6
Sn	13. L	11.	9. L	12. L	17.	13. L	—	—
Sr	150.	186.	150.	211.	180.	120.	100.	300.
Th	2.7	14.	16.	12.	15.	10.	4.7	12.
U	3.5	4.4	4.5	4.7	8.9	3.6	1.8	3.7
V	150.	142.	119.	127.	143.	150.	100.	300.
Y	23.	35.	26.	42.	33.	37.	10.	26.
Yb	3.	5.	5.	5.	5.	5.	1.	2.6
Zn	80.	88.	57.	106.	117.	133.	39.	95.
Zr	185.	253.	164.	210.	192.	307.	30.	160.

Note: L means less than value shown.

SOURCE: Medlin (1977).

TABLE A1.14 Elemental Content of Lurgi Ash from Illinois #6 Coal

Parts per million					
	<10,000	<1,000	<100	<10	
≥10,000	≥1,000	≥100	≥10	≥1	<1
Al	Mg	B	Be	As	Ag
Ca	Mn	Ba	Co	Br	Au
Fe	Na	Ce	Cu	Eu	Cd
K	S	Cl	Cs	F	Hg
Si	Ti	Cr	Ga	Ge	Se
		Rb	La	Hf	
		Sr	Li	Lu	
		V	Mo	Sb	
		Zn	Ni	Ta	
		Zr	Pb	Tl	
			P	W	
			Sc	Yb	
			Th		
			U		

SOURCE: Griffin et al. (1978).

TABLE A1.15 Chemical Composition of H-Coal Vacuum-Still Bottoms from Illinois #6 Coal

Parts per million				
≥ 10,000	< 10,000 ≥ 1,000	< 1,000 ≥ 100	< 100 ≥ 10	< 10
Al	B	Ba	As	Ag
Ca	Cl	Cr	Be	Au
Fe	Mg	F	Br	Cd
K	Na	Li	Ce	Dy
S	P	Mn	Co	Eu
Si	Ti	Rb	Cs	Hf
		Sr	Cu	Hg
		V	Ga	In
		Zn	Ge	Lu
		Zr	La	Sb
			Mo	Sm
			Ni	Sn
			Pb	Ta
			Sc	Yb
			Se	
			Th	
			U	
			W	

SOURCE: Griffin et al. (1978).

TABLE A1.16 Elemental Concentration of Once-Through Ash-Pond Discharges

	Plant A (Fly Ash Pond)			Plant A (Bottom Ash Pond)			Plant B (Fly Ash Pond)			Plant B (Bottom Ash Pond)		
	Min	Avg	Max	Min	Avg	Max	Min	Avg	Max	Min	Avg	Max
Flow (l/sec)[a]	196	392	555	284	1,019	1,451	—	—	—	—	—	—
Total Alkalinity (mg/l as $CaCO_3$)[a]	—	—	—	30	85	160	6	54	72	17	78	226
Phen. Alkalinity (mg/l as $CaCO_3$)[a]	0	0	0	0	0	0	0	3	19	5	45	176
Conductivity (µmho / cm)[a]	615	810	1,125	210	332	910	160	242	490	310	650	1,600
Total Hardness (mg/l as $CaCO_3$)[a]	185	261.5	520	76	142	394	60	108	225	125	302	505
pH[a]	3.6	4.4	6.3	4.1	7.2	7.9	6.5	8.0	9.5	5.0	9.8	11.3
Dissolved Solids (mg/l)[a]	141	508	820	69	167	404	5	142	2,123	84	524	812
Suspended Solids (mg/l)[a]	2	62.5	256	5	60	657	7	64	2,523	7	85	470
Aluminum (mg/l)	3.6	7.2	8.8	0.5	3.5	8.0	0.1	1.8	4.8	0.4	2.8	8.6
Ammonia (mg/l as N)	0.02	0.43	1.4	0.04	0.12	0.34	<0.01	0.07	0.20	<0.01	0.09	0.31
Arsenic (mg/l)	<0.005	0.010	0.023	0.002	0.006	0.015	<0.005	0.03	0.065	<0.005	0.018	0.055
Barium (mg/l)	0.2	0.3	0.4	<0.1	0.2	0.3	<0.1	0.1	0.2	<0.1	0.1	0.3
Beryllium (mg/l)	<0.01	0.01	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cadmium (mg/l)	0.023	0.037	0.052	<0.001	0.001	0.002	<0.001	0.001	0.002	<0.001	0.003	0.01
Calcium (mg/l)	94	136	180	23	40	67	27	142	430	16	63	200
Chloride (mg/l)	5	7	14	5	8	15	4	6	8	5	7	11
Chromium (mg/l)	0.012	0.067	0.17	<0.005	0.009	0.023	<0.005	0.02	0.036	<0.005	0.01	0.026
Copper (mg/l)	0.16	0.31	0.45	<0.01	0.065	0.14	<0.01	0.02	0.04	<0.01	0.041	0.18
Cyanide (mg/l)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Iron (mg/l)	0.33	1.44	6.6	1.7	5.29	11	0.19	1.93	7.1	0.26	5.98	30
Lead (mg/l)	<0.01	0.06	0.2	<0.01	0.02	0.03	<0.010	0.01	0.03	<0.01	0.02	0.05
Magnesium (mg/l)	9.4	14	20	0.3	5.9	9.3	0.2	3.9	6.8	4.1	6.9	21
Manganese (mg/l)	0.29	0.48	0.63	0.07	0.16	0.26	0.02	0.13	0.63	0.02	0.58	3.6
Mercury (mg/l)	<0.0002	0.0003	0.0006	<0.0002	0.0007	0.0026	<0.0002	0.001	0.0056	<0.0002	0.001	0.0026
Nickel (mg/l)	0.06	1.1	0.13	0.05	<0.05	0.12	<0.05	0.05	0.08	<0.05	0.12	0.14
Total Phosphate (mg/l as P)	<0.01	0.02	0.06	<0.01	0.08	0.23	<0.01	0.08	0.18	0.03	0.07	0.12
Selenium (mg/l)	<0.001	0.002	0.004	<0.001	0.002	0.004	<0.001	0.015	0.064	<0.001	0.011	0.056
Silica (mg/l)	10	12.6	15	6.1	7.4	8.6	3.7	8	22	3.7	7.7	22
Silver (mg/l)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Sulfate (mg/l)	240	358	440	41	49	80	35	209	480	22	139	470
Zinc (mg/l)	1.1	1.51	2.7	0.02	0.09	0.16	<0.01	0.06	0.13	0.02	0.14	0.55

Note: In those cases where a minimum value was less than detectable, the average was calculated using a substituted value which was equal to one-half the value of the detectable limit.

The reported values include background concentrations in the raw water supply. To assess environmental impacts that may be attributed to ash pond effluents, background concentrations would have to be subtracted from these values.

Data gathered in 1973-1974.

[a] Weekly grab samples. All others quarterly grab samples.

TABLE A1.16 (Continued)

	Plant C (Combined Ash Pond)			Plant D (Combined Ash Pond)			Plant E (Combined Ash Pond)			Plant F (Combined Ash Pond)		
	Min	Avg	Max	Min	Avg	Max	Min	Avg	Max	Min	Avg	Max
Flow (1/sec)[a]	232	463	622	52	558	290	357	382	420	1,451	2,079	2,524
Total Alkalinity (mg/1 as $CaCO_3$)[a]	24	71	140	35	58	97	42	154	230	33	113	173
Phen. Alkalinity (mg/1 as $CaCO_3$)[a]	0	0	0	0	5	19	26	114	200	21	96	150
Conductivity (μmho / cm)[a]	195	495	713	233	264	380	285	817	1,150	450	855	1,250
Total Hardness (mg/1 as $CaCO_3$)[a]	25	208	350	68	124	183	76	288	400	88	301	400
pH[a]	6.4	7.1	7.8	7.6	8.6	9.3	10.2	11.2	11.5	10.5	11.2	11.4
Dissolved Solids (mg/1)[a]	124	363	524	40	151	375	135	380	522	12	452	1,410
Suspended Solids (mg, 1)[a]	1	42	202	3	21	120	2	12	43	1	39	182
Aluminum (mg/1)	0.3	1.8	3.8	0.3	1.4	2.9	1.1	2.4	4.5	0.8	2.0	3.1
Ammonia (mg/1 as N)	0.02	0.11	0.23	0.01	0.07	0.15	0.03	0.05	0.09	0.03	0.15	0.38
Arsenic (mg/1)	<0.005	0.013	0.050	0.010	0.03	0.050	<0.005	0.005	0.130	<0.005	<0.005	0.005
Barium (mg/1)	<0.1	0.2	0.4	<0.1	0.2	0.3	<0.1	0.2	0.4	<0.1	0.2	0.5
Beryllium (mg/1)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cadmium (mg/1)	0.002	0.005	0.010	<0.001	0.001	0.002	<0.001	0.001	0.003	<0.001	0.001	0.002
Calcium (mg/1)	45	82	100	26	32	37	64	129	200	74	115	160
Chloride (mg/1)	8	12	16	3	4	5	4	6	9	4	5	6
Chromium (mg/1)	<0.005	0.005	0.008	<0.005	0.004	0.008	<0.005	0.019	0.039	0.012	0.043	0.072
Copper (mg/1)	<0.01	0.03	0.07	<0.01	0.01	0.04	<0.01	0.08	0.19	<0.01	0.02	0.04
Cyanide (mg/1)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Iron (mg/1)	0.33	2.1	4.1	0.08	0.25	0.55	0.05	0.30	0.95	<0.05	0.23	1.10
Lead (mg/1)	<0.01	0.02	0.07	<0.01	0.01	0.02	<0.01	0.014	0.07	<0.01	0.01	0.04
Magnesium (mg/1)	1.4	10.0	16.0	7.5	8.3	9.0	0.1	0.4	1.1	0.2	2.0	7.2
Manganese (mg/1)	0.13	0.22	0.34	<0.01	0.03	0.05	<0.01	0.01	0.02	<0.01	0.01	0.04
Mercury (mg/1)	<0.0002	0.015	0.11	<0.0002	0.0002	0.001	<0.0002	0.0002	0.0003	<0.0002	0.038	0.300
Nickel (mg/1)	<0.05	<0.05	0.07	<0.05	0.05	0.19	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Total Phosphate (mg/1 as P)	<0.01	0.05	0.08	<0.01	0.03	0.08	<0.01	0.01	0.02	<0.01	0.03	0.08
Selenium (mg/1)	<0.001	0.014	0.08	<0.002	0.065	0.14	<0.002	0.009	0.011	0.009	0.016	0.028
Silica (mg/1)	4.7	7.0	8.7	1.0	3.7	4.8	5.0	6.6	8.4	4.2	6.1	7.6
Silver (mg/1)	<0.01	0.01	0.03	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Sulfate (mg/1)	110	155	190	16	59	84	70	136	170	14	156	240
Zinc (mg/1)	0.02	0.12	0.25	<0.01	0.03	0.07	<0.01	0.05	0.08	<0.01	0.04	0.08

Note: In those cases where a minimum value was less than detectable, the average was calculated using a substituted value which was equal to one-half the value of the detectable limit.

The reported values include background concentrations in the raw water supply. To assess environmental impacts that may be attributed to ash pond effluents, background concentrations would have to be subtracted from these values.

Data gathered in 1973-1974.

[a] Weekly grab samples. All others quarterly grab samples.

TABLE A1.16 (Continued)

	Plant G (Combined Ash Pond)			Plant H (Combined Ash Pond)			Plant I (Combined Ash Pond)			Plant J (Combined Ash Pond)		
	Min	Avg	Max	Min	Avg	Max	Min	Avg	Max	Min	Avg	Max
Flow (l/sec)[a]	158	547	631	2	181	212	0	469	1,512	236	873	1,523
Total Alkalinity (mg/l as $CaCO_3$)[a]	20	47	72	20	70	100	70	150	317	0	41	96
Phen. Alkalinity (mg/l as $CaCO_3$)[a]	2	22	44	0	14	25	50	126	290	0	<1	9
Conductivity (μmho/cm)	295	394	500	220	406	500	280	618	1,400	215	312	550
Total Hardness (mg/l as $CaCO_3$)	150	196	360	80	114	155	30	209	420	65	105	152
pH[a]	8.2	9.6	10.5	7.3	8.5	9.6	10.5	11.3	12.0	3.3	6.3	8.8
Dissolved Solids (mg/l)[a]	210	279	381	100	268	365	142	270	470	66	197	294
Suspended Solids (mg/l)[a]	1	20	64	3	18	290	2	22	102	2	140	431
Aluminum (mg/l)	0.4	1.8	2.9	0.8	1.6	2.9	0.8	1.6	3.3	0.4	2.7	7.6
Ammonia (mg/l as N)	0.01	0.04	0.10	0.03	0.45	2.6	0.02	0.06	0.22	<0.01	0.05	0.08
Arsenic (mg/l)	<0.005	0.029	0.070	0.035	0.10	0.18	<0.005	0.005	0.005	<0.005	0.038	0.110
Barium (mg/l)	<0.1	0.2	0.3	<0.1	0.2	0.3	<0.1	0.2	0.4	<0.1	0.2	0.3
Beryllium (mg/l)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cadmium (mg/l)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.001	0.002
Calcium (mg/l)	25	78	110	34	47	67	53	103	170	23	37	57
Chloride (mg/l)	2	4	8	8	14	22	4	6	8	2	3	4
Chromium (mg/l)	<0.005	0.012	0.023	<0.005	0.006	0.010	0.010	0.024	0.042	<0.005	0.006	0.007
Copper (mg/l)	<0.01	0.03	0.09	<0.01	0.05	0.14	<0.01	0.05	0.11	0.02	0.06	0.18
Cyanide (mg/l)	<0.01	0.01	0.02	<0.01	<0.01	<0.01	<0.01	0.01	0.02	<0.01	<0.01	<0.01
Iron (mg/l)	0.27	0.95	4.6	0.22	0.63	1.4	0.06	0.29	0.76	0.1	2.3	9.4
Lead (mg/l)	<0.01	0.01	0.02	<0.01	0.01	0.03	<0.01	0.01	0.01	<0.01	0.02	0.04
Magnesium (mg/l)	1.1	2.5	4.6	5.8	7.4	8.8	0.2	0.4	0.6	3.9	6.5	9.3
Manganese (mg/l)	<0.01	0.05	0.23	0.02	0.05	0.08	<0.01	0.01	0.02	0.05	0.39	0.68
Mercury (mg/l)	<0.0002	0.0008	0.0026	<0.0002	0.0006	0.0016	<0.0002	0.0002	0.0011	<0.0002	0.0003	0.0008
Nickel (mg/l)	<0.05	<0.05	<0.05	<0.05	0.05	0.07	<0.05	<0.05	<0.05	<0.05	0.05	0.07
Total Phosphate (mg/l as P)	0.01	0.05	0.09	0.04	0.12	0.21	<0.01	0.02	0.06	0.01	0.05	0.13
Selenium (mg/l)	<0.001	0.010	0.018	<0.002	0.013	0.028	<0.002	0.004	0.008	<0.001	0.003	0.006
Silica (mg/l)	3.9	4.8	5.7	2.7	4.8	5.6	7.1	8.1	8.7	3.5	6.2	7.9
Silver (mg/l)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Sulfate (mg/l)	55	133	190	45	88	140	50	76	140	90	122	170
Zinc (mg/l)	<0.01	0.03	0.07	<0.01	0.04	0.15	<0.01	0.08	0.30	0.02	0.05	0.12

Note: In those cases where a minimum value was less than detectable, the average was calculated using a substituted value which was equal to one-half the value of the detectable limit.

The reported values include background concentrations in the raw water supply. To assess environmental impacts that may be attributed to ash pond effluents, background concentrations would have to be subtracted from these values.

Data gathered in 1973-1974.

[a] Weekly grab samples. All others quarterly grab samples.

TABLE A1.16 (Continued)

	Plant K (Combined Ash Pond)			Plant L (Combined Ash Pond)		
	Min	Avg	Max	Min	Avg	Max
Flow (l/sec)[a]	284	1,249	2,456	505	887	1,167
Total Alkalinity (mg/l as $CaCO_3$)[a]	58	96	187	52	92	214
Phen. Alkalinity (mg/l as $CaCO_3$)[a]	15	75	151	1	44	204
Conductivity (µmho /cm)	270	469	720	110	314	870
Total Hardness (mg/l as $CaCO_3$)[a]	118	174	242	105	239	320
pH[a]	9.4	10.8	11.4	8.0	10.5	11.5
Dissolved Solids (mg/l)[a]	23	232	416	91	219	338
Suspended Solids (mg/l)[a]	2	14	59	0	18	92
Aluminum (mg/l)	0.5	1.7	2.4	1.3	2.1	2.6
Ammonia (mg/l as N)	0.02	0.06	0.16	0.06	0.64	1.3
Arsenic (mg/l)	<0.005	0.012	0.025	0.010	0.036	0.070
Barium (mg/l)	<0.1	0.2	0.3	<0.1	0.1	0.2
Beryllium (mg/l)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cadmium (mg/l)	<0.001	<0.001	<0.001	<0.001	0.001	0.004
Calcium (mg/l)	52	87	130	32	55	91
Chloride (mg/l)	7	12	19	4	6	9
Chromium (mg/l)	0.014	0.021	0.026	<0.005	0.008	0.012
Copper (mg/l)	<0.01	0.05	0.10	<0.01	0.04	0.14
Cyanide (mg/l)	<0.01	<0.01	0.01	<0.01	<0.01	<0.01
Iron (mg/l)	0.11	0.24	0.34	0.38	0.69	1.0
Lead (mg/l)	<0.01	0.025	0.04	<0.01	0.01	0.04
Magnesium (mg/l)	0.4	1	3.0	1.3	3.1	4.2
Manganese (mg/l)	<0.01	0.01	0.02	<0.01	<0.01	0.01
Mercury (mg/l)	<0.0002	0.0004	0.0008	<0.0002	0.0003	0.0009
Nickel (mg/l)	<0.05	0.07	0.22	<0.05	<0.05	<0.05
Total Phosphate (mg/l as P)	<0.01	0.02	0.06	0.01	0.07	0.15
Selenium (mg/l)	<0.002	0.011	0.016	<0.002	0.010	0.014
Silica (mg/l)	6.5	7.4	8.8	5.0	5.6	6.7
Silver (mg/l)	<0.01	<0.01	< 0.01	<0.01	<0.01	0.01
Sulfate (mg/l)	55	87	110	55	85	110
Zinc (mg/l)	<0.01	0.05	0.11	0.02	0.04	0.06

Note: In those cases where a minimum value was less than detectable, the average was caluculated using a substituted value which was equal to one-half the value of the detectable limit.

The reported values include background concentrations in the raw water supply. To assess environmental impacts that may be attributed to ash pond effluents, background concentrations would have to be substracted from these values.

Data gathered in 1973-1974.

[a] Weekly grab samples. All others quarterly grab samples.

SOURCE: Chu et al. (1976).

APPENDIX B--TECHNICAL PROGRAM OF WORKSHOP ON ACCESSORY ELEMENTS IN COAL

A workshop on Accessory Elements in Coal was organized by the Coal Panel of the Committee on Accessory Elements, National Research Council, and held on March 1, 1977 at the National Academy of Sciences, Washington, D.C. The technical program, designed to provide information on the distribution of accessory elements from increased utilization of coal, covered the following topics:

Geochemistry and Petrology and Their Relationships to Accessory Elements
    F.T.C. Ting, Department of Geology and Geography, West Virginia University
Variation in Coal Composition by Major Basin
    J.H. Medlin, U.S. Geological Survey
Organic and Inorganic Affinities of Accessory Elements in Coal
    H.J. Gluskoter, Illinois State Geological Survey
Accessory Elements in Coal-Preparation Wastes and Effects of Possible New Cleaning Procedures on the Nature of Such Wastes
    C.T. Ford, Bituminous Coal Research, Monroeville, Pennsylvania
Environmental Implications of Coal-Conversion Processes
    C.W. Gehrs, Oak Ridge National Laboratory, Oak Ridge, Tennessee
Removal of Accessory Elements from Coal
    E.J. Mezey, Battelle Columbus Laboratories, Columbus, Ohio
Composition and Utilization of Coal Wastes
    J.G. Rose, University of Kentucky
Removal and Recovery of Accessory Elements from Coal and Coal Wastes
    E.M. Wewerka, Los Alamos Scientific Laboratory
Solubility, Attenuation, and Toxicity of Accessory Elements in Coal Wastes and Leachates
    R.A. Griffin, Illinois State Geological Survey
Economic Considerations in the Recovery and Disposal of Accessory Elements in Coal
    R.T. Newcomb, West Virginia University
Near-Surface Accumulation of Accessory Elements Around Two Western Power Plants
    J.J. Connor, U.S. Geological Survey
Effects of Utilization of Western Coals on Redistribution of Accessory Elements
    C.C. Gordon, University of Montana
Redistribution of Accessory Elements in Underground Gasification
    C.F. Brandenburg and D.D. Fischer, Laramie Energy Research Center, U.S. Energy Research and Development Administration
Gases in Coal: Their Origins, Properties and Behavior
    F.J. Radd, Continental Oil Company

Some speakers presented materials extemporaneously or from brief notes and slides; others presented information from informal papers.

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REDISTRIBUTION OF ACCESSORY ELEMENTS AND COMPOUNDS FROM MINING AND PROCESSING OF OIL SHALE

SUMMARY

The primary goal of this report is to evaluate the potential for the redistribution of minerals from oil shale mining, processing, and related disposal activities. The oil shale resource has not been developed and therefore the approach is qualitative, describing the redistribution of accessory elements for representative extraction processes, and identifying potential problems and gaps in knowledge with recommendations for further study. The assessment has focused on the Green River Formation in northwestern Colorado, northeastern Utah, and southwestern Wyoming, which is estimated to contain 1.8 trillion barrels of oil. Although much of this oil will probably never be economically recoverable because of the low oil content of some of the raw shale, competition from coal-liquefaction and other products, or for other reasons, a substantial production of shale oil is likely and will bring a variety of problems to producers.

Particular emphasis is placed in this report on oil shale extraction in the Piceance Creek Basin, which contains most of the oil in the Green River Formation and for which the most detailed information is available. For typical development sites and processes in the Piceance Creek Basin, the assessment initially summarizes (1) the basic mineralogy and the elements subject to redistribution in pertinent stratigraphic zones and (2) the hydrology and chemical composition of ground and surface waters. With this background, elemental redistributions to be expected as a result of oil shale mining, retorting, recovery of accessory minerals, partial refining, and disposal are defined for specific processes. From comparisons of background information with knowledge derived from pilot- and large-scale retort operations, possible site-specific and regional environmental problem areas are identified. General informational and research needs are discussed in terms of process effluents, atmospheric and hydrologic transport, and environmental effects.

The oil shale of the Green River Formation is mainly dolomite containing varying but relatively high concentrations of an insoluble organic material referred to as kerogen. The kerogenic units are interbedded with tuffs, siltstones, claystones, and sandstones, and locally contain halite (NaCl), nahcolite ($NaHCO_3$), and disseminated

dawsonite [$NaAl(OH)_2CO_3$]. Nahcolite and dawsonite are potential resources of soda ash and aluminum, particularly at the depositional centers of the Piceance Creek Basin.

Trace elements receiving detailed consideration in this study are Sb, As, Be, B, Cd, F, Li, Hg, Mo, and Se. The highest concentrations (median >25 parts per million) of As, B, F, Li, and Mo are found in raw shale. From the limited information available, elemental concentration does not appear to differ markedly in relation to stratigraphic position or geographic locality.

The Piceance Creek Basin is a structural basin, and ground water generally flows from recharge areas at the margins to discharge areas near the center. Low recharge rates lead to low flow rates, which in turn result in considerable leaching of the strata and salt enrichment of the waters. The Basin contains several surface drainage areas ultimately draining to the Colorado River. These surface- and ground-water systems are intimately related and have an integrated effect on the Colorado River.

The total dissolved solids in ground water range from 400 to 24,000 milligams per liter. The concentrations of some elements in the ground water prior to development exceed public health standards, which may have a marked effect on interpretation of the effects of the developing industry. Waters may require treatment prior to use or discharge, influencing redistribution of accessory elements. Sulfur is characteristically high, and chlorine, fluorine, and boron may be elevated depending upon location and aquifer.

The carbonate-rich sedimentary rocks of the Basin, in conjunction with low rainfall, lead to relatively high concentrations of total dissolved solids in surface waters, ranging from approximately 300 to 5,000 milligrams per liter, depending upon location and flow rate. As in the case of ground water, certain constituents, including S, F, Cl, Fe, As and Mn, may exceed public health standards at times.

Major phases of oil shale extraction that may involve redistribution of accessory elements include mining of the shale, extraction of the shale oil, recovery of accessory minerals, prerefining, and disposal of processed shale and waters.

Mining

Mining methods may be categorized as: (1) open-pit, in which shale is extracted by dragline after removal of overburden; (2) room-and-pillar, in which shale is removed by loader after selective rubblization (breaking into small rock fragments), leaving pillars of shale for support; and (3) rubblization *in situ*, in which retorting is accomplished underground. Mining methods with greatest potential for initial commercialization, at present, appear to be room-and-pillar and modified *in situ* methods, in which a portion of the shale is removed to the surface.

Open-pit mining is economically attractive for some surface and near-surface oil shales since essentially 100 percent of the oil shale can be recovered, compared to a maximum of 50 to 70 percent of the mineable zone for underground mines. In underground mining, it is estimated that 30 to 50 percent of the shale in the mined zone would be left unmined by the room-and-pillar technique, which would be used largely in high-grade shales, with the pillars likely candidates for eventual further mining. Both open-pit and underground mining might require the disposal of highly saline ground water, depending upon the location.

Primary wastes associated with mining operations are the overburden from open-pit mining and mine dewatering wastes from both open-pit and room-and-pillar mining. Deep open-pit mining can produce large volumes of such wastes: a hypothetical mine might produce as much as 35 billion cubic feet (bcf) of overburden (i.e., material that must be removed prior to mining the economic shale deposits), and more than 370 billion cubic feet of low-grade unusable shale. In general, oil shale beds having a stripping ratio of 1:2 (i.e., 1 foot of overburden to 2 feet of extractable shale) are considered economical, and even lower ratios may be acceptable. Primary problems in the disposal of overburden include leaching of soluble minerals and erosion during temporary storage following mining, and revegetation following closure of open-pit mines.

Extraction of Shale Oil

Two basic retorting modes are under development for the separation of oil from raw shale--underground (*in situ*, modified *in situ*) and aboveground (surface retorts).

Modified In Situ Processes

The modified *in situ* operations that are planned involve vertical or horizontal underground retort chambers. Because rock rubblized by conventional mining methods expands by about 25 percent in volume, about 75 percent of the mined oil shale would be processed underground. The remaining 25 percent would be moved to the surface and processed by surface retorts.

Information regarding trace-element redistribution resulting from modified *in situ* retorting is limited to laboratory tests simulating *in situ* pyrolysis conducted by the U.S. Department of Energy, Laramie Energy Research Center, and Lawrence Livermore Laboratories.

Assuming that the retort chamber is sealed from communication with permeable underground zones either naturally, or by use of a backfill of slurried retorted shale from surface retorting, redistribution of elements in an *in situ* retort chamber is limited to the pyrolysis products pumped from the retort as gases and liquids. The solids remain in the retort chamber, except for a small quantity of suspended particles in the liquid. In the modified *in situ* process, surface retorting will also be necessary.

The composition of the gaseous products from retorting of oil shales of uniform composition depends on the retort temperature and the composition of the air used to support combustion. Low-Btu gas (60 to 120 Btu/ft^3) produced in the retort is composed of a mixture of combustion gases and noncondensable hydrocarbons from kerogen pyrolysis. The elements present in the gas are primarily N, C, O, H, and S; the compounds are primarily nitrous oxides, carbon dioxide, carbon monoxide, sulfur dioxide, hydrogen sulfide, low-molecular-weight hydrocarbons, and water vapor.

Trace-element content of the gas phase from the in situ process is not available; however, analyses of oil and retorted shale indicate mercury, arsenic, and fluorine may exist in the gas phase. The water vapor condensed from the gas phase contains, primarily, ammonia and carbonates, with traces of organic substances and sulfur-containing compounds.

Low-Btu gas has been proposed for use in generating electrical power. Efficient combustion of these gases in a turbine would produce nitrous oxides, sulfur dioxide, carbon dioxide and water in the off-gases, which would probably be emitted to the atmosphere at the plant site. Treatment will be required if combustion emissions exceed state standards.

Shale oil composition from the in situ retort is similar to that produced from the gas combustion surface retort. Elements detected in the oil from simulated in situ retort tests include As, Cd, F, Se, S, N, Fe, Ni, Pb, Hg, P, and Ti. The redistribution of these elements would be governed by subsequent use and the refining process.

In situ process demonstrations have reportedly produced greater amounts of water than surface retorts. This water, not fully characterized at present, contains mainly ammonia, carbonate and bicarbonate, sodium, sulfate, chloride, and dissolved or suspended organic compounds (e.g., phenolics, amines, organic acids, hydrocarbons, and mercaptans). Smaller quantities of calcium, magnesium, and sulfides exist along with suspended shale fines. Trace elements present in retort water from simulated in situ tests include As, B, F, Hg, Se, and S. Retort waste water may require purification before being discharged to the surface.

A new and totally different set of potential problems will exist if the retort chamber is not sealed and is in communication with ground water. In addition to possible mobilization of shale constituents, rubblization using a mixture of ammonium nitrate and fuel oil as an explosive will result in enrichment in nitrogen, largely as nitrate. Nitrate is highly soluble and is therefore a potentially important ground-water contaminant.

Surface Retort Processes

Surface retorting will result in elemental redistribution into gaseous and liquid phases as in the case of in situ methods, but considerable quantities of retorted shale will also be produced. Available qualitative information indicates that most of the trace elements, including Be, Cd, Cr, Co, F, Pb, Mn, Mo, Ni, V, and Zn, are conserved in the retorted shales. However, As, Ni, V, and Zn are redistributed to the oil in significant quantities. Arsenic, mercury, iron, chromium, and zinc are detected in off-gases. Of the macroelements, carbon, nitrogen, and sulfur are also redistributed to the oil and gaseous phases. Particulate emissions during crushing and conveyoring of the raw shale may also result in elemental redistribution, perhaps off-site. Due to its high concentration (median levels of 1,200 parts per million) in the raw shale, fluorine would likely be an important element in particulate emissions.

Recovery of Accessory Minerals

Significant reserves of nahcolite and dawsonite exist in the thick lower-zone oil shales of the Green River Formation. These are expected to yield the bulk of the accessory mineral products from the Piceance Creek Basin oil shales. These resources are believed to be economically accessible by a surface outcrop. Industry has estimated that a mine producing 25,500 tons per day of raw shale could yield, daily, 15,000 barrels of oil, 700 tons of alumina, 1,500 tons of soda ash, and 4,400 tons of nahcolite.

Raw nahcolite is unchanged chemically by the mechanical process of crushing, sorting, and screening. There are apparently no commercially attractive concentrations of metals in dawsonitic oil shale other than aluminum, which is removed by a leaching process that may result in some redistribution of associated elements in leach waters, depending upon the disposal method adopted. The concentrations and redistribution of other elements would otherwise be similar to those described for surface retorting except that the removal of commercial minerals may significantly reduce the volume of retorted shale to be disposed of.

Partial Refining

Although physicochemical properties vary with the type of retorting process used, the pour point, viscosity, and nitrogen content of shale oils are significantly higher than in most crude petroleums. The high pour point makes transportation by pipeline or tanker unlikely without heating or treatment. Thus, retorting complexes may ultimately have prerefining facilities on-site to reduce viscosity and pour point. Sulfur and nitrogen compounds tend to "poison" heavy metal catalysts used in refining processes. Undesirable sulfur and nitrogen may be removed from the shale oil before pipeline transport by hydrotreating on-site to the extent that water supplies permit. Developers' plans entail varying degrees of prerefining on-site, depending on transportation and marketing needs.

A proposed retorting complex would include holding tanks for storage of the crude oil, a distillation column, a delayed coker, hydrotreaters for nitrogen and sulfur removal, a Claus reactor for sulfur recovery, a steam reformer for hydrogen generation, and product clean-up facilities. Such a complex could produce partially refined, low-sulfur, low-nitrogen premium crude (syncrude), as well as commercially valuable sulfur, ammonia, and coke.

Disposal of Wastes

Redistribution of accessory elements during oil shale processing will occur principally as a result of waste disposal. Three major types of solid and liquid waste may be disposed to the ground from aboveground retorting. These include off-gas scrubbing wastes, retorted shale, and retort process water. In addition, prerefinery wastes may also be generated. Because of the quantities produced, disposal of retorted shale will result in major redistribution of accessory elements.

Off-Gas Scrubber Wastes

Off-gases, containing carbon, nitrogen, and sulfur and volatile trace-elements will be produced by retorting, and wastes from scrubber treatments of the off-gases may be disposed to the ground. At present, little information on the composition and consequences of disposal of these wastes is available.

Retorted Shale

The quantity of retorted shale produced by a 1 million barrel-per-day mature industry has been estimated to be 1.2 to 2.0 million tons per day. Disposal may result in redistribution of accessory elements through loss of particulates by wind and water erosion, and leaching of retorted shale.

The porosity of unmined oil shale is low (<5 to 10 percent) compared to that of compacted retorted shale, which ranges up to 40 percent by volume depending on the amount of compaction. Thus, complete disposal of retorted shale in the original mines is not possible except perhaps after recovery of nahcolite and dawsonite as byproducts in some locations. Surface disposal will therefore be required.

Unless stabilized, retorted shale is subject to water and wind erosion. Embankments must be carefully engineered and compaction of shale and establishment of vegetative cover will be required to minimize erosion over the long term. Successful implementation of these treatments requires that the net movement of water be downward to avoid transport of salts from the retorted shale to the overlying soil, and, to assure this, initial leaching of the retorted shale may be required.

Retorted shale contains nominal quantities of oxides, which range from soluble (sodium) to slightly soluble (calcium and magnesium). The conversion of largely insoluble carbonates and other minerals to the more soluble oxides depends on the retorting temperature. Carbonates begin to decompose at 600°F, and at 1,500°F conversion is largely complete; heating rate and time are also important factors. Thus, the leachability of these elements will depend on the source of the shale and the retorting process. Disposal of retorted shales close to the water table or within the saturated zone would, however, present a potential mechanism for redistribution of elements and a possible source of ground-water pollution. It appears that, except for arsenic, fluorine, mercury, and perhaps antimony, most trace elements are conserved in the retorted shale, with lesser quantities in the shale oil. Only limited information is available on the leachability of elements from the retorted shale and its potential impact.

As in the case of inorganic components, the concentrations of organic residuals depend upon the source of the shale, retorting temperatures, oxygen concentration, and reaction kinetics. Thus, potential problems related to organic residues, such as complexing of trace elements and solubilization of the organic residues, will depend on the process and the management of the wastes as well as environmental variables, such as changes in temperature and moisture with time. The effects of these variables on mobility of organic residues has not been studied.

A particular concern relating to retorted shale leaching processes is the potential impact of oil shale development on the salinity of the Colorado River system. Oil shale development in the Piceance Creek Basin could affect Lower Colorado River Basin salinity through a number of mechanisms. The withdrawal of low-salt ground or surface waters from the Upper Basin for use in oil shale production could reduce the flow of diluting water and increase Lower Basin salinity. Estimates of the amounts of such increases, and comparisons with increases caused by other uses, have been made. The predicted net change of about 2 to 3 percent is considerably smaller than changes estimated for irrigation and anticipated transmountain diversions to the east slope of the Rockies. Uncontrolled mine dewatering, runoff from retorted shale disposal piles, or percolation of leachate into ground-water/surface-water systems would also increase Lower Basin salinity. Drought in some years may be expected to intensify these effects. Conversely, the withdrawal, for shale industry use, of more highly saline waters (>400 milligrams per liter) from saline aquifers or from the highly saline surface streams of the shale region could proportionately decrease the salinity of the Colorado River.

A quantitative analysis of the effects of the addition of salts as a result of oil shale operation is difficult to determine at present, due to the uncertainties associated with the type and timing of the shale processing technologies likely to be used, the reliability of catchment basins against failure, or the amount of percolation through ground-water/surface-water systems. These factors and the possible mitigating effects of proper waste management and engineering design are under intensive study.

Retort Wastes

Water incorporated in the raw shale is released during the retorting process. The composition of this water has not been well established. However, it contains relatively high concentrations of soluble carbon and, likely, polar organic nitrogen compounds. Several programs are under way which should provide, in the near future, information necessary to evaluate the possible redistribution of elements by disposal of this material and its possible uses by industry, such as for retorted shale wetting and dust control.

Prerefining Wastes

Wastes from prerefinery distillation, coking, hydrogen/steam reforming, hydrogenation, and kiln processes would be similar to the wastes produced by these processes in the petroleum industry. Spent heavy-metal catalysts, (e.g., Zn, Co, Mo, Fe, Cr, and Cu), diatomaceous earth, caustic-wash solutions, coke, deactivated carbon, and extracted arsenic are wastes likely to result from prerefinery processes, and the quantities produced have been estimated. Petroleum coke is the principal product, in addition to oil, likely to be used outside the oil shale region. Coke need not be produced, however, because the residual fraction of the oil from which it is derived could be burned as fuel oil. This residual fraction contains most of the trace elements.

Information Needs

The production of shale oil involves a unique technology with respect to processing, nature of product, and geography. Information necessary for a thorough evaluation of the effect of the several technologies with commercial potential on redistribution of accessory elements and associated environmental effects is not complete and/or fully available in the open literature as required for independent assessment. Further evaluation of the redistribution of accessory elements and the environmental impact of methods for producing shale oil is necessary as quantitative information accumulates. This information is pertinent to questions of siting, control technology, licensing, and regulation, which, in turn, may strongly affect production strategy.

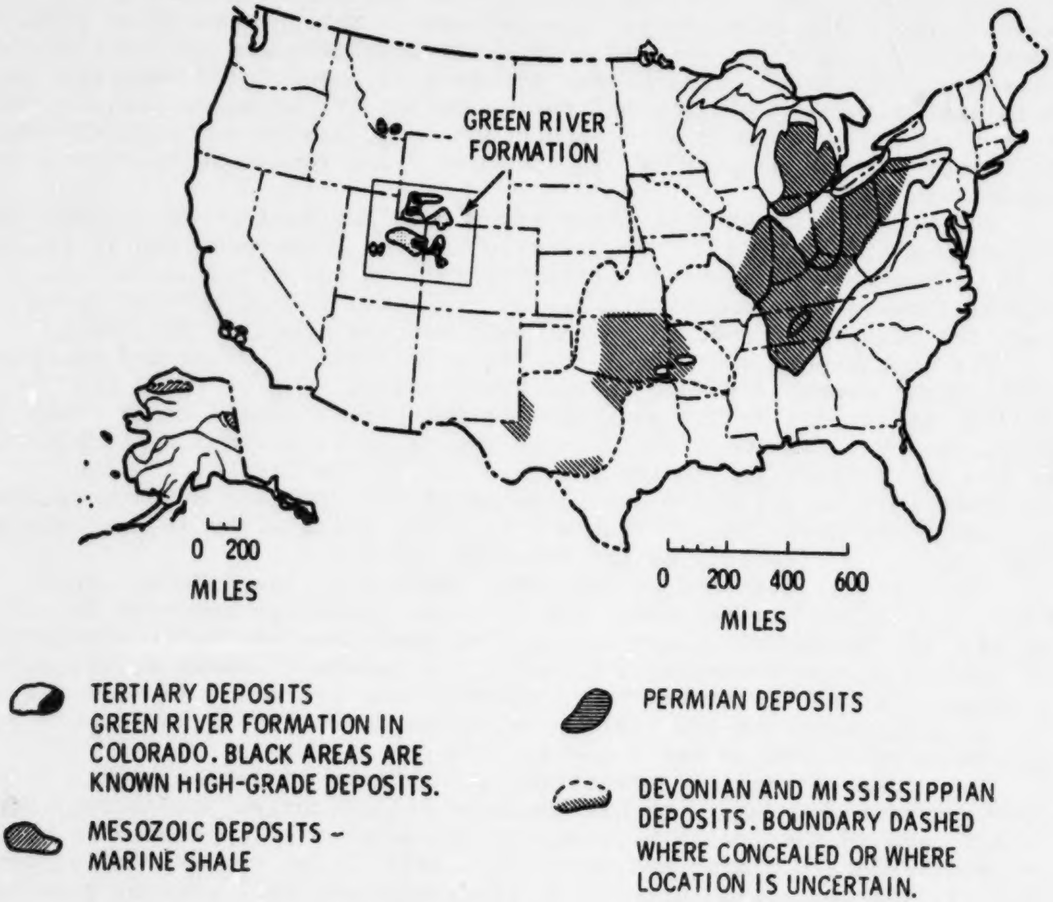
Future study of the redistribution of accessory elements, and of associated environmental and health problems, through a balanced, interdisciplinary research effort should include: source characterization and process-stream monitoring, atmospheric transport, hydrologic transport, and environmental effects over the long term. Further research and assessment should take full cognizance of the unique characteristics of the region, including the natural background levels of inorganic and organic substances compared to levels resulting from redistribution by oil shale development. Efforts are under way in industry, federal agencies and their contractors, and the universities to meet these needs. However, there is a need to collect, catalog, and evaluate pertinent data from past efforts in shale, coal, and mineral processing, for use as a basis for early coordination of future research.

INTRODUCTION

Large-scale mining of oil shale and construction and operation of oil shale processing facilities would result in some direct atmospheric emissions and in the production of waste water and solid wastes. The influx of employees for an oil shale industry and attendant support services would also have an impact on air, water, and land resources (Crawford et al. 1976). However, the primary goal of this report is to identify and evaluate the potential for the redistribution of minerals, particularly trace elements, and to a lesser extent, of organic residuals from oil shale mining, processing, and related disposal activities. A secondary goal is to identify possible environmental consequences arising from redistribution.

The oil shale industry has developed a number of potentially commercial processes, but not all have been fully evaluated and information is not yet available for some process and disposal operations. Furthermore, much of the information available on trace-elements has been developed relatively recently by industry, and, although published information was used wherever possible in this report, unpublished data were used extensively in the discussion of some technologies. For these reasons, the approach in this study has been largely qualitative, involving description of the redistribution of accessory elements for representative extraction processes, identification of potential problems and of gaps in knowledge, and recommendation of areas for further study.

Oil shale deposits occur in many parts of the world. In the United States, they occur as lacustrine rocks, marine black shales, and carbonaceous shales associated with coal-bearing strata (Figure 2.1). When these shales are crushed and retorted, volatile hydrocarbons are driven off that may be recovered as crude oil and gas. Yields range


GREEN RIVER FORMATION
0 200
MILES
0 200 400 600
MILES
TERTIARY DEPOSITS GREEN RIVER FORMATION IN COLORADO. BLACK AREAS ARE KNOWN HIGH-GRADE DEPOSITS.
PERMIAN DEPOSITS
MESOZOIC DEPOSITS - MARINE SHALE
DEVONIAN AND MISSISSIPPIAN DEPOSITS. BOUNDARY DASHED WHERE CONCEALED OR WHERE LOCATION IS UNCERTAIN.

SOURCE: Modified from Duncan and Swanson (1965).

FIGURE 2.1 Oil shale deposits of the United States.

from as high as 160 gallons of oil per ton of rock in Alaskan tasmanite shales down to a few gallons per ton in the low-grade but extensive Devonian shales in the eastern United States.

The oil shales of greatest current economic potential occur within the Green River Formation in northwestern Colorado, northeastern Utah, and southwestern Wyoming. This formation is estimated to contain a total of 1.8 trillion barrels of oil (Donnell 1964, and Donnell and Blair 1970). The Piceance Creek Basin of northwestern Colorado (Figure 2.2) and the Uinta Basin of eastern Utah have been for the past half century the loci of most of the interest and effort of industry and government, and, for the Piceance Creek Basin, in particular, which contains most of the identified resources in the Green River Formation (1.2 trillion barrels), extensive information is available. This report thus focuses on the effects of oil shale extraction in the Piceance Creek Basin. Several development sites representative of the Basin are considered in detail, although future development is not limited to this region.

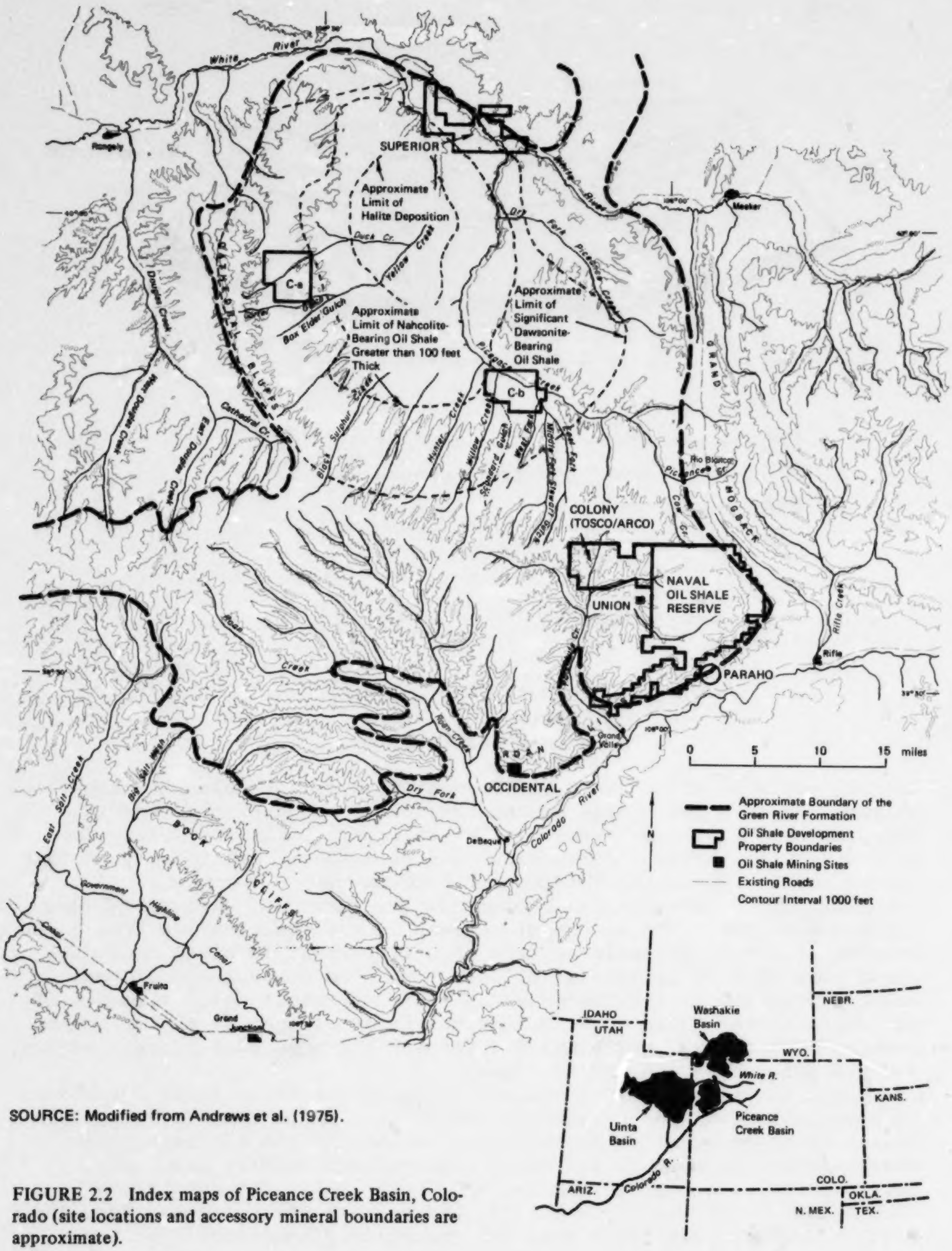
The Green River Formation (Figure 2.3) was deposited about 50 million years ago in extensive Eocene lakes. Thicknesses up to 2,000 feet of continuous oil-bearing rocks have been measured in parts of the Piceance Creek Basin. The eroded remnants of these thick deposits have been geologically mapped in an area exceeding 17,000 square miles. They have received hydrologic study and mineralogic analysis. Subdivisions and water-bearing properties of the Green River Formation are given in Table 2.1.

The Piceance Creek Basin is a structural basin; rock units that crop out around its margins dip downward toward the structural center (Figure 2.3). Ground-water movement generally follows the structure of the Basin, flowing from recharge areas at the margins to discharge areas near the structural center, in the north-central part of the Basin.

The topographic surface of the Basin is a broad, dissected plateau containing several drainage areas (see Crawford et al. [1976] and Andrews et al. [1975] for detailed treatment of Piceance Creek Basin physiography). The northern part of the Basin is drained by tributaries of the White River, including Piceance and Yellow Creeks, and the southern part is drained by tributaries of the Colorado River including Parachute and Roan Creeks (Figure 2.2). The White River drains into the Green River, a tributary of the Colorado River.

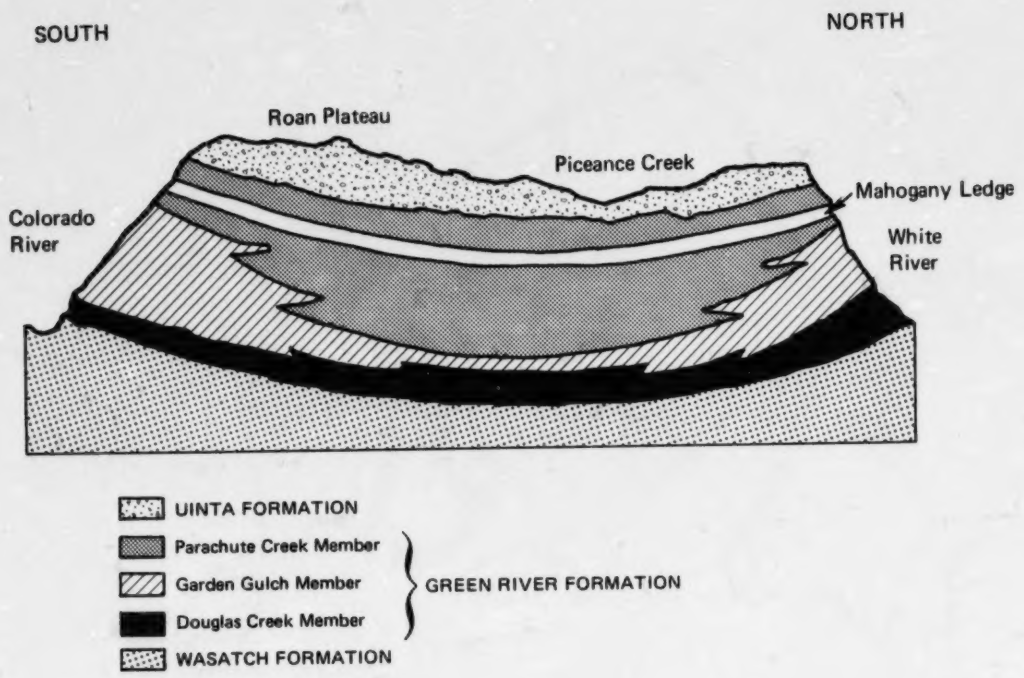
The surface-water and ground-water systems of the Piceance Creek Basin are intimately related. Ground-water discharge accounts for 80 percent of the annual runoff volume, and dominates the water chemistry of streams except during spring runoff and snowmelt (Weeks et al. 1974). Detailed discussions of the basic hydrogeology are found in Weeks et al. (1974) and Andrews et al. (1975). Piceance Creek drains the most extensive watershed in the formation (Figure 2.2).

The Basin is semiarid, receiving about 12 to 16 inches of precipitation per year. It has immature soils, sparse vegetation, high relief, and is particularly vulnerable to erosion as evidenced by many incised, eroded valleys (Andrews et al. 1975). The vegetation reflects man's influence through grazing of livestock, and tall grasses grow only on irrigated valley floors. Natural grasslands have been replaced by sagebrush, serviceberry, mountain mahogany, scrub oak, greasewood, rabbit brush, and other shrubs.



SOURCE: Modified from Andrews et al. (1975).

FIGURE 2.2 Index maps of Piceance Creek Basin, Colorado (site locations and accessory mineral boundaries are approximate).



SOURCE: Modified from U.S. DOI (1977).

FIGURE 2.3 Diagrammatic section across the Piceance Creek area.

GREEN RIVER OIL SHALE

Mineralogy

The oil shale of the Green River Formation is mainly dolomite containing varying but relatively high concentrations of an insoluble organic material referred to as kerogen. The kerogenic units are interbedded with tuffs, siltstones, claystones, and sandstones, and locally contain halite ($NaCl$), nahcolite ($NaHCO_3$), and disseminated dawsonite [$NaAl(OH)_2CO_3$]. Nahcolite and dawsonite are potential sources of soda ash and aluminum. The amount of kerogen in the shale varies from a few percent in low-grade shale to more than 40 percent in shale that will yield more than 75 gallons of oil per ton. The composition of the organic fraction in the Mahogany Zone (the uppermost, rich sequence of oil shale in the Green River Formation) is approximately 80.5 percent carbon, 10.3 percent hydrogen, 2.4 percent nitrogen, 1.0 percent sulfur, and 5.8 percent oxygen (Smith 1961).

The basic mineralogy of the oil shale in the Green River Formation is remarkably uniform throughout, except that major concentrations of saline minerals near the depositional centers of the Piceance Creek Basin are not present at its edge. Mineralogic studies have been conducted on both surface (Brobst and Tucker 1973) and subsurface (Desborough et al. 1974, Dyni 1974, and Keighin 1975) samples from the Basin. However, limitations of the analytical techniques used have

TABLE 2.1 Detailed Stratigraphy and Water-Bearing Characteristics of the Green River Formation, Piceance Creek Basin, Colorado

Geologic Unit	Unit Subdivisions		Lithologic Description	Hydrologic Unit	Water-Yielding Properties
Valley Alluvium 0' - 140'	—		Sand, gravel, clay	Alluvial Aquifer	Limited in areal extent and thickness. 1500 gpm maximum.
Uinta Formation 0' - 1250'	—		Mainly sandstone and siltstone with minor amounts of low-grade oil shale and barren marlstone.	Upper Aquifer	Well yields ≥ 100 gpm. TDS from 250 to 1800 ppm.
Green River Formation	Parachute Creek Member 500' - 1600'	Upper Part of Parachute Creek Member			
		Mahogany Zone	Moderate- to high-grade oil shale.	Aquitard	Low permeability. Limited percolation through vertical fracture is important in regional ground-water flow.
		Leached Zone	Low- to high-grade oil shale.	Lower Aquifer	Best developed in north central part of basin. Confined aquifer. Wells may yield 1000 gpm <2000 ppm TDS* near edges to 45,000 ppm TDS near center.
		High-resistivity or Saline Zone	Saline minerals and moderate- to high-grade oil shale	Aquitard	Relatively impermeable.
	Garden Gulch member 0' - 900'		Mainly clayey shale and low- to moderate-grade oil shale.	Aquitard	Relatively impermeable
	Douglas Creeek member 0' - 800'		Mainly sandstone with minor amounts of limestone.	Minor Aquifer	Relatively impermeable. ≤ 50 gpm well yields. TDS from 3000 to 12,000 ppm.
	Anvil Points member 0' - 1670'		Shale, sandstone, marlstone.	Minor Aquifer	Relatively impermeable.
Wasatch Formation				Aquitard	Relatively impermeable.

*TDS = Total dissolved solids.

TABLE 2.2 Minerals Present in Major Stratigraphic Zones of the Piceance Creek Basin (see Table 2.1)

Zone	Major Minerals	Lesser Minerals	Minor Minerals
Overburden	Quartz Dolomite	Analcime Calcite Albite K-Feldspar	Illite Pyrite Siderite Aragonite
Mahogany	Dolomite Quartz	Albite Calcite	K-Feldspar Aragonite Siderite Illite Pyrite Analcime Dawsonite
Leached	Dolomite Albite Quartz Illite	K-Feldspar Calcite	Pyrite Siderite (Analcime Dawsonite)
Saline	Nahcolite Dolomite Quartz	Halite Dawsonite Albite K-Feldspar	Pyrite Calcite (Siderite Illite)
Garden Gulch Member	Quartz Dolomite	Albite Illite	Pyrite Calcite K-Feldspar (Siderite Analcime)

SOURCE: Brobst and Tucker (1973), Desborough et al. (1974), Dyni (1974), and Keighin (1975).

permitted only estimates of the relative abundance of the minerals. These studies indicate that near the margin of the Basin and outside of the line of significant dawsonite deposition (Figure 2.2) there are two zones of differing mineralogy: (1) the overburden above the Mahogany Zone, and (2) the Mahogany Zone and underlying oil shales (Table 2.1). The major minerals in these zones are quartz and dolomite (Table 2.2).

Near the center of the Basin, within the line indicating the limit of significant dawsonitic oil shale (Figure 2.2), there are five zones of differing mineralogy: (1) the overburden above the Mahogany Zone; (2) the Mahogany Zone; (3) the leached zone; (4) the saline zone; and (5) the Garden Gulch Member of the Green River Formation (Figure 2.3, and Table 2.1). The basic mineralogy of the overburden and of the Mahogany Zone is similar to that described for the Basin margin. The major minerals present in the leached and Garden Gulch zones include dolomite and quartz, but nahcolite predominates in the saline zone.

The maximum area of deposition of significant amounts of halite, nahcolite, and dawsonite, occurring in the saline zone, is approximately 500 square miles (Figure 2.2). In the outer area, aluminum may be derived from dawsonite and an unidentified aluminum-bearing substance; however, near the edge of the Basin, in an acid leach, additional aluminum, along with silica, can be derived from analcime, albite, and potassium feldspar.

Major Elements

Desborough et al. (1974) reported the concentrations of the major elements and their probable mineralogical residence in the raw shale. The analyses were based on four cores from drill holes through rich beds in the Mahogany Zone and the underlying R-4 zone in the Piceance Creek Basin, and on two cores from the Mahogany Zone in the Uinta Basin. The results of this study are outlined in Table 2.3. In addition to Si and Al present largely in quartz and albite, the shale contains Fe, Mg, Ca, K, and Na as components of other minerals. The concentration of sulfur in kerogen in these shales ranges up to 1.2 weight percent; as sulfide in pyrite it ranges up to 2.2 weight percent (Desborough et al. 1974). Similar concentrations of these elements were present in a composite sample from the Mahogany Zone in Utah (Smith and Stanfield 1964).

Trace Elements Subject to Redistribution

The selection of trace elements for detailed attention in this study was based on concentration, mobility, and possible toxicity to the ecosystem and man. Detailed consideration was given to Sb, As, Be, B, Cd, F, Li, Hg, Mo, and Se.

Semiquantitative spectrographic analyses of trace elements have been conducted on samples from the Mahogany Zone of the Uinta Basin and from both the Mahogany Zone and lower oil shale zones in the Piceance Creek

TABLE 2.3 Concentration of Selected Elements and Their Probable Mineral Residences in Raw Shale from the Piceance Creek and Uinta Basins

Element	Range in Concentration (Weight Percent as oxide)	Principal Minerals
Silicon	25-41	Quartz, albite, feldspar, analcime
Aluminum	4-10	Albite, dawsonite, feldspar, analcime, amorphous material
Iron	2-4	Pyrite, dolomite, siderite
Magnesium	1-8	Dolomite, calcite
Calcium	3-4	Calcite, dolomite
Potassium	1-2.5	Feldspar
Sodium	1-2.5	Dawsonite, albite, analcime
Phosphorus	0.05-0.8	Apatite

SOURCE: Desborough et al. (1974).

Basin. More precise analytical methods were used for many of the trace elements deemed to be most significant in raw shale from cores drilled on the federal lease tracts (Desborough et al. 1974; Poulson and Jensen 1975; Shendrikar and Faudel 1978; Tract C-b Oil Shale Project 1975; B.E. Weichman, Superior Oil Co., written communication, 1977). The results are shown in Table 2.4.

Although there is a large range in the reported amounts of boron and fluorine in raw shale, this evidently reflects the actual variation in concentration of these elements. In contrast, the reported differences in concentration of arsenic, cadmium, selenium, and antimony are frequently greater between individual laboratories than between oil shale samples (J.R. Donnell, USGS, written communication, March 1977; Rio Blanco Oil Shale Project 1975). Earlier reported mercury values would likely be viewed as maximum values, as recent investigations (Donnell and Shaw 1977) have indicated that interferences and perhaps contamination have resulted in erroneously high mercury values for oil shales. Further study of this element is necessary.

Arsenic, B, F, Li and Mo are present in the highest concentrations. With the possible exception of arsenic, these may be expected to be relatively soluble. Also, arsenic, boron, and fluorine are likely to be volatile. On the basis of present information there do not appear to be major differences in elemental concentration related to stratigraphic position or geographic locality.

Typical Development Sites and Processes

Lease tracts, companies holding the leases, and retorting processes considered typical of the Piceance Creek Basin are summarized in Table 2.5. Their locations are shown in Figure 2.2.

TABLE 2.4 Concentrations of Selected Trace Elements in Oil Shale from Several Locations

Element	Concentration (ppm)	
	Range	Median
Arsenic	4.6 - 120.0	28.0
Beryllium	0.18 - 5.6	1.0
Boron	5.0 - 300.0	66.0
Cadmium	0.08 - 2.98	0.7
Fluorine	300.0 - 3400.0	1162.0
Lithium	5.1 - 300.0	37.0
Selenium	0.2 - 14.6	2.0
Molybdenum	3.0 - 200.0	30.0
Mercury	0.1 - 2.9	0.4
Antimony	0.29 - 3.0	1.0

SOURCE: Desborough et al. (1974); Poulson and Jensen (1975); Tract C-b (1975); B.E. Weichman, Superior Oil Co., written communication (April 1977); Shendrikar and Faudel (1978).

TABLE 2.5 Representative Tracts, Companies, and Processes Typical of the Piceance Creek Basin

Tract[a]	Mining Method	Retort Process	Companies
1. Colony	Room-and-Pillar	TOSCO II	ARCO/TOSCO
Naval Reserve	Room-and-Pillar	Paraho	DEI
2. C-b	Rubblization	In situ	Ashland/ Occidental
3. Superior	Room-and-Pillar	Circular Grate	Superior

(a) See Figure 2.2 for locations.

Mining methods may be categorized as: (1) open-pit, in which shale is extracted by dragline after removal of overburden; (2) room-and-pillar, in which shale is removed by loader after selective rubblization, leaving pillars of shale for support; and (3) rubblization in situ, in which most of the broken shale is left in the ground and retorted in place. Mining methods with greatest potential for initial commercialization, at present, appear to be room-and-pillar and modified in situ methods, in which a portion of the shale is removed to the surface. Two basic retorting modes are under development for the separation of oil from raw shale--underground (in situ, modified in situ) and aboveground (surface retorts).

Three or more private companies and two government agencies are conducting research on modified in situ processes. All of them propose Mahogany Zone oil shale for initial development, and at least two propose development in the Piceance Creek Basin. The modified in situ operations that are planned involve vertical or horizontal underground retort chambers. Since rock rubblized by conventional mining methods expands by about 25 percent in volume, about 75 percent of the mined oil shale would be processed underground. The remaining 25 percent would be moved to the surface and processed by surface retorts. It is possible, therefore, that there would be limited redistribution of soluble constituents due to leaching of the raw shales brought to the surface and due to leaching of the resulting retort wastes.

Surface retorts of current interest are of two types: those heated by combustion of retort products and those heated by indirect means (Atwood 1975, and Schora et al. 1977). The first category includes the Paraho Direct Mode and the Superior Circular Grate (direct) retorts. The second category includes the TOSCO II, Superior Circular Grate (indirect), Union Type B, Paraho Indirect Mode, and the Lurgi retorts. The Lurgi process encompasses both indirect retorting with hot shale ash and combustion of the carbonaceous retorted shale to produce the heated ash. Volatilization of trace metals may result from either retorting process.

Colony Development Property

This property contains the richest exposed oil shale in the Piceance Creek Basin. The oil shale of immediate interest is in a layer about 60 feet thick within the Mahogany Zone and will yield an average of about 35 gallons of oil per ton. The Mahogany Zone is exposed in much of this area, and the oil shale may be mined by conventional room-and-pillar methods through a horizontal entry. Both above and below this layer are several hundred feet of shale of lesser value that may be of commercial interest in the future. The area is characterized by deeply incised canyons with as much as 3,000 feet of topographic relief. There is very little ground water in or adjacent to the oil shale.

The Colony property is typical of several hundred square miles of land in the southern part of the Piceance Creek Basin. Paraho Development Corporation and Occidental Oil Company are conducting research in this region (locations in Figure 2.2). Conditions on this property are also quite similar to those on the federal oil shale tracts, U-a and U-b, in the eastern part of the Uinta Basin, Utah.

Federal Oil Shale Lease Tract C-b

This tract contains continuous oil shale sequences more than 1,000 feet thick. For several hundred feet below the Mahogany Zone the oil shale contains considerable quantities of finely disseminated dawsonite.

The land surface within the tract is dissected by a series of parallel or subparallel northeast-trending streams, and topographic relief is 300 to 500 feet from valley bottoms to ridge tops. Ground water is contained in three aquifers: the alluvium, the combined Uinta and upper Green River Formation, and that part of the Green River Formation immediately below the Mahogany Zone.

Access to the Mahogany Zone for conventional room-and-pillar mining or modified in situ recovery would be through a vertical shaft at least 700 feet deep. Tract C-b is typical of a larger oil shale area of several hundred square miles, intermediate in both geographic location and depth between the exposed oil shale at the margin of the Basin and the deeply buried, rich oil shales at its center. Conditions similar to this exist on much of the federal land in the Piceance Creek Basin.

Superior Oil Company Property

This is one of the few areas where there are well-developed surface exposures of the thick, rich oil shale below the Mahogany Zone. Considerable quantities of disseminated dawsonite occur through several hundred feet of oil shale. Moderate amounts of nahcolite are present in the southern part of the tract and on adjacent federal land.

Though topographic relief is generally lower here than on tract C-b, in places it may exceed 500 feet. Ground water exists in the aquifers that are present on tract C-b.

Mining of the lower oil shale zone, which also contains nahcolite and dawsonite, may be initiated at the outcrop and continued through an inclined shaft along beds that dip a maximum of 10°. However, a saline aquifer of nearly basin-wide extent occupies the interval between these lower shales and the Mahogany Zone, perhaps requiring special mining methods. Multi-mineral recovery methods that might be developed on this property would be applicable over an area of several hundred square miles in the Basin. Therefore, this area is of considerable importance from the standpoint of redistribution of accessory elements.

GROUND WATER IN THE PICEANCE CREEK BASIN

Ground water throughout the Basin is part of a regional flow system that is in a state of hydrologic equilibrium. Most ground-water recharge occurs at the Basin margins; the ground water flows to discharge areas in the north-central part of the Basin, near its structural center. Piceance Creek Valley is the major discharge area (Weeks et al. 1974). Because of the close interrelationship between surface water and ground water, any natural or man-made modification of quality or quantity in one leads to at least some modification in the other.

There are three principal aquifer systems in the Basin. These are: (1) the stream valley alluvial soils; (2) the upper aquifer, immediately above the Mahogany Zone; and (3) the lower aquifer, immediately below the Mahogany Zone (Figure 2.3, Table 2.1). These aquifer systems are of importance in terms of (1) the effect of oil shale development on their water quality and the quality of receiving waters, (2) the possible necessity for mine dewatering, and (3) their potential as sources of water for processing and reclamation. All other rock units within the Green River Formation are relatively impermeable but allow ground water to move, in time, from the recharge areas to points of discharge. Thus, the Mahogany Zone, though a good aquitard, is not an impermeable barrier to ground-water flow. The difference in hydrostatic head between the upper and lower aquifers is less than 100 feet in most places, and the total head difference within the regional flow system is about 1,200 feet (Weeks et al. 1974).

For water supply or dewatering purposes that result in stress on the hydrologic system over a relatively short period, aquifer characteristics are significant (see Weeks et al. [1974] for descriptions of these characteristics). With respect to water quality, however, flow-system characteristics are more important: it is during its long residence time in the soils and rocks of the Basin that the ground water acquires its chemical characteristics.

Low recharge rates in the Basin lead to a low ground-water flow rate. Leaching of the more soluble components of the sediments in the Green River Formation takes place, and salts, including macro-ions and trace elements, are mobilized. The most soluble minerals are concentrated in the interior of the Basin (Figure 2.2) where the ground water tends to have larger concentrations of sodium and chloride. The ground water near the periphery of the Basin is dominated by bicarbonate. The range of concentrations of common ions in the main aquifers, the Uinta and Parachute Creek members, are given in Appendix Figures A2.1 and A2.2.

Natural concentrations of some trace elements in the ground water are above recommended public health standards (Hem 1970). This may have a marked effect on interpretation of the effects of development. It may also influence the redistribution of accessory elements because waters in parts of the Basin may require treatment prior to use, and, in dewatering, treatment may be required prior to discharge.

On the Colony Development property, the total dissolved solids (TDS) in three alluvium samples have been shown to range between 400 and 1,000 mg/l (G.J. Saulnier, USGS, written communication, March 1977). The TDS in water from seven drill holes in the Uinta and Green River aquifers ranged from 500 to 2,110 mg/l and exceeded 1,000 mg/l in two of the holes. The TDS in water from 13 holes in the Uinta Formation and the upper Parachute Creek Member on the Federal Oil Shale Lease Tract C-b ranged from 500 to 3,079 mg/l, and seven exceeded 1,000 mg/l. The TDS in water from nine holes in the lower Parachute Creek Member (leached zone) at this location ranged from 708 to 45,500 mg/l (G.J. Saulnier, USGS, written communication, March 1977; and Tract C-b Oil Shale Project, 1975). Higher concentrations were noted in the Basin center where the strata contain elevated salt levels. On the Superior Oil Company property, the TDS in four holes in the combined Green River aquifers ranged from 3,240 to 73,600 mg/l (G.J. Saulnier, USGS, written communication, March 1977; and Weichman 1974a).

The chemical characteristics of ground water prior to significant development at these sites are summarized in Appendix Tables A2.1, A2.2, and A2.3. Elements present in significant concentrations are listed, i.e., those exceeding public health limits (U.S. Public Health Service 1962). Sulfur is characteristically high, and chlorine, fluorine and boron may be elevated depending upon location and aquifer.

SURFACE WATER IN THE PICEANCE CREEK BASIN

As would be expected in an area of carbonate-rich sedimentary rocks and annual rainfall of only 12 to 16 inches, the surface waters of the Piceance Creek Basin have relatively high concentrations of dissolved solids. The seasonal nature of the precipitation also results in considerable variation in the surface-water quality in the Basin (Coffin et al. 1971, Ficke et al. 1974, and Weichman 1974a). The TDS concentrations in Piceance Creek were found to range from 440 to 4,700 mg/l and in Parachute Creek from 360 to 1,280 mg/l. The ranges of concentrations of common ions in these waters at different flow rates are given in Appendix Figures A2.3 and A2.4.

The concentration and composition of dissolved solids in surface waters are influenced by ground-water contributions (Coffin et al. 1971). For example, the upstream stretch of Piceance Creek receives ground water from the Uinta Formation and is dominated by calcium, magnesium, and bicarbonate. Below Thirteen-mile Creek, sodium-rich water from the Parachute Creek Member enters the Piceance Creek, and sodium is the dominant cation below Ryan Gulch (Figure 2.4). The results of specific studies of surface waters of areas selected for detailed examination are given below.

At the Colony Development property, the TDS concentrations have ranged from 500 to 750 mg/l in Davis Creek, in the Middle Fork of Parachute Creek, and in two springs that feed them. The dissolved sulfate concentration has exceeded allowable health standards only in

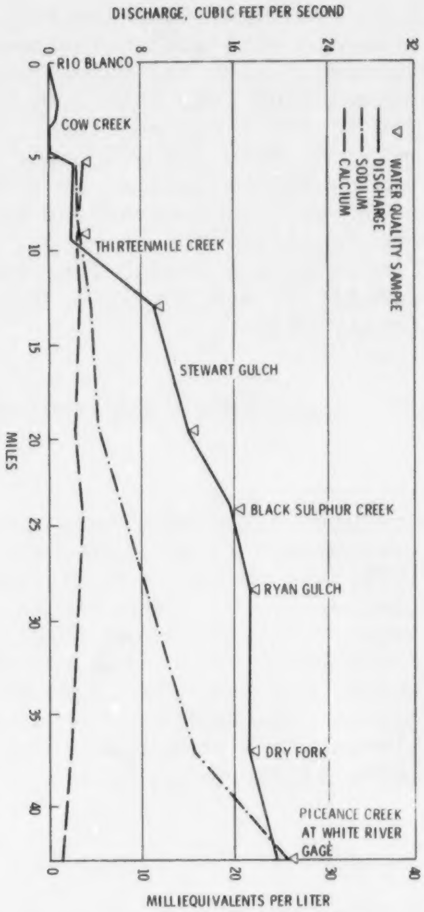


FIGURE 2.4 Changes in water quality accompanying discharges along Piceance Creek, October 6, 1965.

SOURCE: Coffin et al. (1971).

Davis Creek, where at one time in 1970 it reached 274 mg/l (G.J. Saulnier, USGS, written communication, March 1977).

The quality of the water in springs and in the major streams on and near the Federal Oil Shale Lease Tract C-b is routinely monitored (G.J. Saulnier, USGS, written communication, March, 1977; and Tract C-b Oil Shale Project 1975). The TDS concentrations have been below 1,000 mg/l at about half of the sampling sites and ranged between 1,090 and 1,160 mg/l at the remaining sites. Waters at about half of the sampled localities contained less than 250 mg/l dissolved sulfate and the remainder between 310 and 380 mg/l. Fluorine concentrations also exceeded the allowable limit at half the sampled localities, ranging from 1.3 to 35 mg/l. Concentrations of manganese (.11 mg/l) and mercury (.01 mg/l) exceeded public health standards at one locality.

In the case of the Superior Oil Company property, the water in Piceance Creek near the White River has been routinely sampled at the U.S. Geological Survey stream gauging station for several years. Analyses (G.J. Saulnier, USGS, written communication, March 1977; and

B.E. Weichman, Superior Oil Co., written communication, April 1977) indicate that concentrations of sulfate, chloride, and TDS vary inversely with the water volume in the Creek. The TDS concentrations ranged from less than 1,000 to 5,280 mg/l; sulfate ranged from less than 250 to 570 mg/l; and chloride ranged from less than 250 to 1,000 mg/l. Water at this and six other localities within the area considered for mining and processing by Superior has been sampled for trace-element analyses. Concentrations at the USGS gauging station exceeded public health limits for arsenic (.56 mg/l) and magnesium (.3 mg/l). Health limits were exceeded for fluorine (ranging from .7 to 7.0 mg/l) at five localities and for iron (ranging from 1.5 to 2.6 mg/l) at six localities.

ELEMENTS REDISTRIBUTED FROM PROCESSING AND DEVELOPMENT

Retort Products

Raw oil shales have been quantitatively analyzed for trace metals (Desborough et al. 1974, Poulson et al. 1977, Shendrikar and Faudel 1978, and Fruchter et al. 1977), and information on the chemical composition of raw shale is available in the various Environmental Impact Statements and Detailed Development Plans prepared by Colony Development and by the participants in Federal Prototype Oil Shale Leases C-a and C-b. Much of the chemical data was obtained by spark source mass spectroscopy and is semiquantitative. The redistribution of elements and compounds associated with the in situ and surface retorting modes is discussed below.

Modified In Situ Processes

Information regarding trace-element redistribution resulting from modified in situ retorting is limited to laboratory tests simulating in situ pyrolysis conducted by DOE, Laramie Energy Research Center (LERC), and Lawrence Livermore Laboratories (LLL).

Assuming that the retort chamber is sealed from communication with permeable underground zones either naturally, or by use of a backfill of slurried retorted shale from surface retorting, redistribution of elements in an in situ retort chamber is limited to the pyrolysis products pumped from the retort in gaseous and liquid phases. The solids remain in the retort chamber, except for a small quantity of suspended particles in the liquid. In the modified in situ process, surface retorting will also be necessary.

Gas Phase Product

The composition of the gaseous products from retorting of oil shales of uniform composition depends on the retort temperature and the composition of the air used to support combustion. Low-Btu gas (60 to 120 Btu/ft^3) produced in the retort is composed of a mixture of combustion gases and noncondensable hydrocarbons from kerogen pyrolysis.

The elements present in the gas are primarily nitrogen, carbon, oxygen, hydrogen, and sulfur; the compounds are primarily nitrous oxides, carbon dioxide, carbon monoxide, sulfur dioxide, hydrogen sulfide, low-molecular-weight hydrocarbons, and water vapor.

Trace-element content of the gas phase from the in situ process is not available; however, analyses of oil and retorted shale indicate mercury, arsenic, and fluorine may exist in the gas phase and should receive furthur consideration. The water vapor condensed from the gas phase contains, primarily, ammonia and carbonates, with traces of organic substances and sulfur-containing compounds.

Low-Btu gas has been proposed for use in generating electrical power. Efficient combustion of these gases in a turbine would produce nitrous oxides, sulfur dioxide, carbon dioxide and water in the off-gases, which would probably be emitted to the atmosphere at the plant site. Treatment will be required if combustion emissions exceed state standards. Future studies should include analysis of trace elements and other constituents in the product gas stream.

Oil Product

Shale oil composition from the in situ retort is similar to that produced from the gas combustion surface retort. Elements detected in the oil from the LERC simulated in situ retort tests (Poulson and Jensen 1975) include As, Cd, F, Se, S, N, Fe, Ni, Pb, Hg, P, and Ti. The redistribution of these elements would be governed by subsequent use and the refining process.

Water Product

In situ process demonstrations have reportedly produced greater amounts of water than surface retorts. This water, not fully characterized at present, contains mainly ammonia, carbonate and bicarbonate, sodium, sulfate, chloride, and dissolved or suspended organic compounds (e.g., phenolics, amines, organic acids, hydrocarbons, and mercaptans). Smaller quantities of calcium, magnesium, and sulfides exist along with suspended shale fines. Trace elements present in retort water from simulated in situ tests (Dulka and Risby 1976) include As, B, F, Hg, Se, and S. Retort waste water will require purification before being discharged to the surface. This treatment will produce a purified waste water and a concentrated brine, which will require additional control prior to disposal (U.S. EPA 1971).

A new and totally different set of potential problems will exist if the retort chamber is not sealed and is in communication with ground water. In addition to possible mobilization of shale constituents, rubblization using a mixture of ammonium nitrate and fuel oil as an explosive will result in enrichment in nitrogen, largely as nitrate. Nitrate is highly soluble and is therefore a potential ground-water contaminant. Study is required of these potential problems.

Surface Retort Processes

Information on the mobilization of trace elements from the operation of representative surface retort pilot plants is limited. However, three composite raw-shale samples prepared from cores taken at the Colony mine site on Parachute Creek were subjected to Fischer assay analysis (Shendrikar and Faudel 1978) for Sb, As, Be, B, Cd, Cr, Co, Cu, F, Pb, Mn, Hg, Mo, Ni, Se, V, and Zn. Assays to develop material balances were also conducted on both the retorted shale and the oil. However, insufficient water was obtained from the Fischer assay to permit complete analyses, and therefore a water sample from a pilot-plant retort was used for the water analyses. The presence of mercury in the pressure-activated switch on the product gas line precluded accurate mercury analyses of the retort products. Other limitations involve the possibilities of certain volatilized elements reacting with the internal metal surfaces of the retort and of contamination during sample preparation. The procedure appears adequate, however, to determine the extent of vaporization of trace elements and of their accumulation in the oil produced.

The results of the Fischer assay and trace-metal analyses on a single sample (TOSCO 1-164) are shown in Tables 2.6 and 2.7, respectively. The overall recovery of arsenic was about 90 percent; the remaining 10 percent may have been precipitated on the metal portion of the retort. Some selenium and copper may also have been precipitated on the retort since recoveries were 90 to 95 percent. Boron recoveries were also less than 100 percent. With the exception of copper,

TABLE 2.6 Fischer Assay of an Oil Shale Sample from the Colony Mine Site (TOSCO 1-164)

Product	Yield[a]
Oil (lb/ton)	252.4
(gallon/ton)	33.5
API Gravity	25.3
Specific Gravity (g/cc)	0.9024
Gas (lb/ton)	60.5
(scf/ton)	827.3
Water (lb/ton)	27.7
(gallon/ton)	3.3
Spent Shale (lb/ton)	1660.1
Total (lb/ton)	2000.7

(a) Based on 2,000 lbs. of Raw Shale

SOURCE: Reprinted with permission from A.D. Shendrikar and G.B. Faudel (1978) Distribution of trace metals during oil shale retorting. Environmental Science & Technology 12(3):332-334. Copyright by the American Chemical Society.

TABLE 2.7 Trace Element Concentrations in Fischer Assay Fractions (Table 2.6) of an Oil Shale Sample (TOSCO 1-164) from the Colony Mine Site

Element	Concentration ppm Raw Shale	Spent Shale	Oil	Water	Recovery (%)
Arsenic	60.0	60.0	21.0	0.0	87.4
Beryllium	1.0	1.2	0.0	0.0	99.6
Boron	63.3	54.0	0.48	0.55	70.9
Cadmium	1.25	1.50	0.00	0.00	99.6
Chromium	41.7	53.8	0.8	0.004	107.3
Cobalt	6.5	8.0	0.26	0.005	102.7
Copper	47.5	55.0	0.25	0.16	96.2
Fluorine	1162.	1352.	<1.0	2.6	96.6
Lead	29.3	34.5	0.14	0.0	97.8
Manganese	230.	275.	0.05	0.02	99.2
Mercury	0.21	NA(a)	NA	NA	—
Molybdenum	30.0	37.7	0.50	0.006	104.5
Nickel	23.9	27.5	1.4	0.034	96.2
Selenium	14.6	16.7	0.0	0.1	94.9
Vanadium	57.1	70.6	0.48	0.0	102.7
Zinc	65.0	76.0	1.4	0.0045	97.3

(a) NA=Not Available

SOURCE: Reprinted with permission from A.D. Shendrikar and G.B. Faudel (1978) Distribution of trace metals during oil shale retorting. Environmental Science and Technology 12(3):332-334. Copyright by the American Chemical Society.

recoveries were poor for all elements normally considered to be volatile, limiting interpretation. However, Be, Cd, Cr, Co, F, Pb, Mn, Mo, Ni, V, and Zn were recovered almost entirely from the retorted shales. Elements that are likely to appear in the oil in appreciable quantity are arsenic, nickel, and zinc. Methods have been developed for removal of arsenic from shale oil (Meyers 1975, and Burger et al. 1975).

Representative Large-Scale Retort Operations

Laramie Energy Research Center Simulated In Situ Retorts

Raw shale, retorted shale, oil, gas, and process water representing feeds to and products from the LERC above-ground simulated in situ retorts have been analyzed for trace elements (Fruchter et al. 1977). However, the samples selected did not represent an integrated operation, and the data obtained cannot be used to calculate balances. The trace-metal concentrations in raw oil shale, retorted shale, crude shale oil, and process water are shown in Table 2.8. The trace metal content of the gas phase is shown in Table 2.9. The studies demonstrate, qualitatively, that most of the elements are conserved in the retorted shale and that As, Hg, Fe, Cr, and Zn are vaporized.

Colony Development Project Retorts

Tests at the Colony Project on the TOSCO II semiworks plant (1,000 tons per day) indicate that yields are essentially those of Fischer assay, and the mobilization of trace elements and organic compounds can be expected to closely approximate the surface retorting processes discussed above. The TOSCO II process produces high-Btu gas suitable for upgrading to natural gas substitute, and also produces a finely ground, relatively low-alkalinity retorted shale with a carbon residue of about 4 percent (Merino and Crookston 1977). Flue gas released to the atmosphere is first scrubbed for raw-shale particles.

Samples of oil shale, shale oil, and retort water taken at pilot and semiworks plants have been subjected to limited analysis for trace-elements and organic compounds (Appendix Tables A2.4, A2.5 and A2.6).

Paraho Retort

The retort employed by Paraho Oil Shale Demonstration is based on the Gas Combustion Process (Jones 1976; Pforzheimer 1974; and Ruark et al. 1969, 1971) with the addition of a continuous oil shale feeder and a moving grate mechanism to discharge retorted shale.

Process samples taken at various points in the Paraho facility at Anvil Points have been analyzed for trace metals (Appendix Table A2.7). The data (J.B. Jones, Paraho Development Corporation, written communication, 1977) again indicate the mobility of arsenic, sulfur, and nitrogen into the shale oil and retort water.

Superior Oil Company Retort

The Superior Oil Company is developing a multi-mineral process designed to produce raw nahcolite, shale oil, alumina, and soda ash in integrated operations (Weichman 1976). Raw nahcolite is obtained by crushing raw shale and separating the finer particles, predominantly nahcolite, which is more friable than the host rock. Shale oil is obtained from the remaining oil shale by retorting in a circular, traveling grate retort. Alumina and soda ash are obtained by leaching retorted shale, followed by selective precipitation.

Major element and trace-element concentrations in raw shale and in products and effluents related to processing are given in Appendix Tables A2.8 and A2.9. These data do not represent standardized samples at all processing plants and do not permit construction of material balances or direct determination of trace-element mobility, but inferences can be drawn regarding potential problems. The elemental composition does not appear to change appreciably from outcrops to the subsurface, except in the case of aluminum and sodium where the

TABLE 2.8 Elemental Composition of Fractions from Simulated *In Situ* Retorting of Oil Shale

Element	Concentration (ppm)[a]				
	Raw Oil Shale 15 gal/ton	Raw Oil Shale 40 gal/ton	Spent Oil Shale	Crude Shale Oil (Run 13)	Process Water (Run 13)
Na	16,100		23,400	19.4 ±0.4	98 ±1
Fe	20,700	17,400	42,100	30 ±1	<1
Cr	30	21	52	0.04±0.01	<0.02
Co	11	11	21.1	0.37±0.02	0.65 ±0.004
Ni	33	30	70		
Sc	5.3	4.9	9.4	<0.0002	0.0004±0.0001
Ba	320	370	650	<0.014	0.13 ±0.02
Sr	440	490	1,120	<0.090	0.150 ±0.05
La	15.9	16.2	34	0.0009	0.0017
Ce	31	30	62	<0.009	0.100
Pr	3.9		7.5	<0.0013	<0.0006
Nd	15		30	<10	0.055
Sm	2.4		4.90	0.00009	0.00031
Eu	0.43	0.45	0.82	<0.0002	0.00029
Gd	1.9		3.3	<0.00065	0.02
Tb	0.26		0.51	0.00006	0.0011
Ho	0.33		0.78	<0.0002	0.00008
Er	1.0		2.0	<0.008	<0.0015
Tm	0.14		0.36	0.00043	0.003
Yb	0.87	0.8	1.8	<0.0003	0.00036
Lu	0.140	0.18	0.34	<0.00003	0.000090
Hf	0.71	1.2	1.3	<0.004	<0.004
Ta	0.53	0.44	0.8		
Th	4.3	4.4	8.2		
U	7.0	5.6	12.7	0.0049±0.0007	0.35
Rb	66	63	130		
Cs	5.2	5.2	8±	<0.002	0.007 ±0.002
As	81	108	91±	5.00 ±0.04	5.89 ±0.04
Sb	3.5	3.6	3.4	0.008 ±0.001	0.016 ±0.002
Zn	136	100	125	2.70 ±0.08	0.43 ±0.04
Br				0.079 ±0.008	0.28 ±0.01
Se	4.3	6	3.6	0.86 ±0.22	0.98 ±0.76
Hg	0.2	0.1	0.003	0.2 ±0.03	0.39 ±0.05
Ga	4.1	5	11		
Cu	72	56	133		

(a) Analyses by neutron activation and x-ray fluorescence.

SOURCE: Fruchter et al. (1977).

TABLE 2.9 Trace Element Form in Off-gas from the Laramie Energy Research Center 10 Ton-Oil Shale Retort

Element	Form	Concentration (ng/m^3)	
		Before Off-gas Burner	After Off-gas Burner
Arsenic	Gaseous	15,000[a]	1,400
	Particulate	400	2,500
Mercury	Particulate	150	600
	Hg^{++}	1,400	100
	$(CH_3)_2Hg^+$	800	300
	$Hg0+(CH_3)_2Hg$	10	900
Iron	Gaseous	120,000	40,000
	Particulate	6,000	150
Chromium	Gaseous	90,000	35,000
	Particulate	2,000	600
Zinc	Gaseous	40,000	15,000
	Particulate	500	150

(a) Occurs mostly in the form of arsine (AsH_3)

SOURCE: Fruchter et al. (1977).

concentrations reflect their presence in dawsonite and nahcolite outcrops. The redistribution of trace elements in the multi-mineral extraction process is discussed in the next section.

Accessory Minerals

Significant resources of nahcolite and dawsonite exist in the thick lower-zone oil shales underlying the leached and Mahogany Zones within the Parachute Creek Member of the Green River Formation (Tables 2.1 and 2.2; Figures 2.2 and 2.3). Dawsonite resources also exist in the leached zone. These zones are expected to yield the bulk of the accessory mineral products from the Piceance Creek Basin oil shales. These resources are believed to be economically accessible (Weichman 1974b) by a surface outcrop on the Superior Oil Company property. The processing of lower-zone shale is significantly different from the processing of Mahogany Zone shale, and the redistribution of elements from processing lower-zone shale must ultimately be considered.

Retorted shale and retort water from the process proposed by the Superior Oil Company would be disposed as backfill in the mined voids underground. This is believed possible because the volume of the retorted shale may be reduced by removal of accessory minerals. The remaining products would be initially stored on the mine site and then transported to various markets. A mine producing 25,500 tons per day of raw shale could yield approximately 10,000 to 15,000 barrels of oil per day, 700 tons per day of alumina, 1,500 tons per day of soda ash, and 4,400 tons per day of nahcolite (B.E. Weichman, Superior Oil Co., written communication, 1977).

The redistribution of trace elements (Sb, As, B, Cd, F, Li, Hg, and Se) in the Superior Oil Company process has been evaluated sequentially from raw, unprocessed shale, through retorting and leaching, to retorted shale destined for disposal in previously mined areas underground. The redistribution of trace elements during the process sequence is outlined in Appendix Table A2.9.

The trace elements As, B, F, Li, and Mo are present in highest concentrations in raw shale of the lower zone. These elements tend to reside in the retorted shale, with minor quantities being redistributed in the products (Appendix Table A2.9). Raw nahcolite is unchanged chemically by the mechanical process of crushing, sorting, and screening. There are apparently no commercially attractive concentrations of metals in the dawsonitic oil shale other than alumina.

Mercury and fluorine appeared to be more plentiful in raw shales than in comparable retorted shales, tending to verify other studies indicating loss during processing. Mercury appeared to be redistributed to the retort water, the retorted oil, and, to some extent, to the gas phase. The concentration of other trace elements in the retorted shale was similar to that in unmined raw shale, indicating that subsurface disposal of retorted shale as a mine backfill source would not result in initial redistribution of trace elements. However, these elements may be more mobile after processing. Further studies of the abundance of these and other elements are required to determine if differences are real or reflect variability in the same shale zone.

The total daily volumes of each product processed and of the particulate emissions after use of baghouse and covered conveyor control have been estimated on the basis of the volume processed, assumed particle-size distribution, and assumed baghouse filter efficiency (Table 2.10). Airborne particulate emissions of trace elements were estimated from particulate emissions and known concentrations of the elements on a pounds-per-year basis. The applicability of these estimates to actual operations or scaled-up versions is not known. These data suggest that the abundance of fluorine in the raw shale (Appendix Table A2.10) leads to relatively higher levels in the particulate emissions as well.

Studies by industry researchers suggest that fluorine levels could be reduced by the use of wet scrubbers on the nahcolite dehydration kiln and on secondary and tertiary crushers, achieving 85 percent reduction in fluorine-bearing particles generated by processing. Residues would then be disposed of in the retorted shale piles (B.E. Weichman, Superior Oil Co., written communication, 1977). Similar approaches may need to be undertaken for other processes as the industry develops.

Partial Refining

Although physicochemical properties vary with the type of retorting process used, all shale oils tend to be somewhat heavier than petroleum. Although they contain only moderate amounts of sulfur (about .7 percent), the pour point, viscosity, and nitrogen content (approximately 1.8 percent) are significantly higher than in most crude petroleums. The high pour point makes transportation by pipeline or tanker unlikely without heating or treatment. The sulfur and nitrogen compounds tend to "poison" heavy-metal catalysts used in refining processes (Sladek 1975b). Thus, retorting complexes may have prerefining facilities on-site to reduce viscosity and pour point. Undesirable sulfur and

TABLE 2.10 Estimated Trace Elements Redistribution from Particulate Emissions During Processing of Oil Shale (Superior Oil Company Single Module Commercial Operation)

Source	Pounds/Day (a)		Pounds/Year from Particulate Emissions									Control Method	Control Eff - %
	Processed	Particulates Released	Sb	As	B	Cd	F	Li	Hg	Mo	Se		
Primary Crusher	56,000,000	56.0	<0.025	0.148	0.158	<0.989	11.87	0.215	nil	0.317	<0.049	Baghouse	99.9
Secondary Crusher	55,944,000	139.9	<0.127	0.762	0.813	<5.08	60.97	0.110	0.002	1.63	<0.254	Baghouse	99.5
Tertiary Crusher	2,596,800	129.9	<0.111	0.667	0.712	<4.50	53.39	1.10	0.002	1.42	<0.225	Baghouse	99.5
Conveyed Raw Shale to Plant	56,000,000	11.4	<0.010	0.062	0.066	<0.413	4.95	0.089	1.85	0.132	<0.021	Baghouse	99.5
Nahcolite Dehydration	8,800,000	435.6	<0.397	0.922	1.59	<15.90	111.3	0.843	0.003	3.34	<0.795	Baghouse	99.0
Alumina Drying Kilns	1,400,000	175.2	<0.160	<0.160	0.639	<6.39	1.92	3.42	0.003	1.09	<0.320	Baghouse	98.5
Soda Ash Drying Kilns	3,000,000	225.6	<0.041	<0.041	<0.823	<8.23	16.47	0.021	0.005	1.32	<0.082	Baghouse	98.5
Conveyors to Storage:													
Nahcolite	8,800,000	34.3	<0.031	<0.031	<0.125	<1.25	10.02	0.066	nil	0.401	<0.063	Covered Conveyor & Baghouse	99.5
Alumina	1,400,000	43.2										Covered Conveyor & Baghouse	99.5
Soda Ash	3,000,000	49.2											
TOTAL	1.97 x 10^8	1300.3											

(a) Assumes 1) 0.1% of particulates from primary crushing would be below 0.1 in. in diameter, and 2) collection efficiency of baghouse filters for particles below 0.1 in. in diameter was 99.9% (manufacturer's estimate).

SOURCE: B.E. Weichman, Superior Oil Co., written communication(1977).

nitrogen may also in some cases be removed from the shale oil before pipeline transport by hydrotreating on site, to the extent that water supplies permit. Current plans are to keep on-site prerefining to a minimum to reduce water requirements.

A proposed retorting complex would include holding tanks for storage of the crude oil, a distillation column, a delayed coker, hydrotreaters for nitrogen and sulfur removal, a Claus reactor for sulfur recovery, a steam reformer for hydrogen generation, and product clean-up facilities (Katell and Wellman 1974). Such a complex could produce partially refined, low-sulfur, low-nitrogen premium crude (syncrude), as well as commercially valuable sulfur, ammonia, and coke.

Wastes from prerefinery distillation, coking, hydrogen/steam reforming, hydrogenation, and kiln processes would be similar to the wastes produced by these processes in the petroleum industry. Spent heavy-metal catalysts, diatomaceous earth, caustic-wash solutions, coke, deactivated carbon, and extracted arsenic are wastes identified in the Colony prerefinery scheme (U.S. DOI 1977). Petroleum coke is the principal product, in addition to oil, likely to be utilized outside the oil shale region. Coke need not be produced, however, as the residual fraction of the oil from which it is produced could be burned as fuel oil. This residual fraction contains most of the trace elements. Trace metals identified in catalyst wastes include Zn, Co, Mo, Fe, Cr, and Cu. Other catalysts are also used, but their identity is proprietary information. For the 50,000-barrels-per-day Colony plant, it is estimated that spent catalyst wastes will average about 715 tons per year (U.S. DOI 1977). Estimated additional wastes include approximately 429 tons per year of diatomaceous earth, 429 tons per year of deactivated carbon, 875 tons per year of caustic wash, 3×10^5 tons per year of coke, and 105 tons per year of extracted arsenic. It is planned that all of the above wastes be mixed into and disposed with retorted shale (20×10^6 tons per year). The prerefinery processes are reasonably standard and the other retorting processes will produce wastes qualitatively similar to those of the TOSCO II process.

MAJOR PROBLEM AREAS

The methods proposed for producing shale oil range from conventional mining and aboveground retorting to *in situ* combustion. The technical and economic aspects of the wide range of options have been studied, but the redistribution of accessory elements and environmental impact of each must also be assessed: questions of siting, control technology, licensing, and regulation can strongly affect the choice of production strategy.

Three major segments inherent in the process of above-ground retorting of shale oil are important in redistribution of accessory elements and have possible environmental consequences. These include mining of the shale, extraction of the shale oil, and disposal and reclamation of processed shale and waters. In mining, aquifer disruption, runoff, and movement of residues downward through the soil to ground water may occur, with possible ultimate impact on streams and rivers. During extraction (crushing, retorting, and refining), redistribution and environmental impacts may result from gaseous emissions and liquid effluents containing organic, saline, and trace-metal residues. Depending upon process and waste management options, disposal of retorted shale may entail the loss of grazing and recreation land, and environmental and human exposure resulting from the movement of particles and leached pollutants to ground and surface waters. The nature and extent of these impacts will depend on control technology and reclamation efforts.

Mining

Open-pit mining is economically attractive for some surface and near-surface oil shales since essentially 100 percent of the economic oil shale can be recovered compared to a maximum of 50 to 70 percent of the mineable zone for underground mines. Surface disturbance is the primary environmental impact of open-pit mining (Ertl 1965). Because of thick overburden, it is likely that a combination of open-pit and underground methods would be used in some places.

Underground mining will probably be accomplished by the room-and-pillar method, in which a portion of the shale is removed, leaving large underground rooms, and the remainder is left in place, to act as pillars to support the overburden. It is estimated that 30 to 50 percent of the shale in the mined zone would be left unmined by this technique, which would be used largely in high-grade shales, with the pillars likely candidates for eventual further mining (East and Gardner 1964 and Sladek 1974). Both open-pit and underground mining might require the disposal of highly saline ground water, depending upon location in the Piceance Creek Basin (Pfeffer and Kerr 1974).

Primary wastes associated with mining operations are the overburden from open-pit mining and mine dewatering wastes from both open-pit and room-and-pillar mining. Deep open-pit mining can produce large volumes of such wastes: a hypothetical mine might produce as much as 35 billion cubic feet of overburden (i.e., material that must be removed prior to mining the economic shale deposits) and more than 370 billion cubic feet of low-grade unuseable shale (Ertl 1965). Open-pit mines have been contemplated for the center of Piceance Creek Basin (Sladek 1975a).

In general, oil shale beds having a stripping ratio of 1:2 (i.e., 1 foot of overburden to 2 feet of extractable shale) are considered economical (Sladek 1975a), and even lower ratios may be acceptable. (Stripping ratios of 1:1 are often acceptable in the mining of coal [Ertl 1965]). Assuming a volume expansion of 25 percent during removal, this represents approximately a 3:1 overburden-to-oil-shale ratio on a volume basis. Primary problems in the disposal of overburden include leaching of soluble matter and erosion during temporary storage following mining, and revegetation following closure of open-pit mines (Fletcher and Baldwin 1973). A substantial amount of research into these problems is being conducted in connection with open-pit mining of coal in the Rocky Mountains area. This research is probably directly applicable to oil shale mining as well (Persse 1975 and Donovan et al. 1976).

Large volumes of potentially economic shale occur below the water table. It may be necessary to dewater these sites before mining. Much of the deeper ground water cannot be discharged to surface waters without treatment. Discharge to the lower aquifer may be an acceptable disposal method for the most highly saline waste (Pfeffer and Kerr 1974).

A particular concern relating to possible future oil shale industrialization is the potential impact on the salinity of the Colorado River system. The present salinity of the Colorado River at several downstream locations is shown in Table 2.11. The values are typical, and the range at any location may be large. For example, concentrations at Imperial Dam, on the Lower Colorado near Yuma, Arizona, may exceed 1,000 milligrams per liter for periods of many days.

Oil shale development in the Piceance Creek Basin could affect Lower Colorado River Basin salinity through a number of mechanisms. The withdrawal of low-salt Upper Basin ground or surface waters for use in oil shale production would increase Lower Basin salinity by reducing dilution. Estimates of the amounts of such increases, and comparisons with increases caused by other uses, have been made. It has been estimated (U.S. DOI 1976), for example, that each 10,000 acre-feet of low-salt water withdrawn in the Upper Colorado River Basin would increase the salinity at Imperial Dam by about 1 mg/l. It has also been estimated (Andrews et al. 1975) that a 1-million-barrel-per-day oil shale industry, using 300,000 acre-feet per year of Upper Basin water with a salt concentration of 400 mg/l, would increase the present average salinity at Imperial Dam (850 mg/l) by about 20 mg/l. The net change of about 2 to 3 percent is considerably smaller than changes estimated for irrigation and anticipated transmountain diversions to the east slope of the Rockies. Uncontrolled mine dewatering, runoff from retorted shale disposal piles, or percolation of leachate into groundwater/surface-water systems would also increase Lower Basin salinity.

TABLE 2.11 Salinity of the Colorado River at Several Locations

Location	Total Dissolved Solids (mg/l)
Headwaters in Colorado	<50
Near Glenwood Springs, Colo., 30 miles upstream from Piceance Creek Basin	310
Parachute Creek (80% of time)	680
Cameo, Colorado, 30 miles below Piceance Creek Basin center	440
Lee Ferry, Arizona	610
Hoover Dam, Arizona-Nevada Border	745
Imperial Dam, Nevada-California Border	850

SOURCE: U.S. DOI (1973).

Drought in some years may be expected to intensify these effects. Conversely, the withdrawal, for shale industry use, of more highly saline waters (>400 mg/l) from saline aquifers or from the highly saline surface streams of the shale region, could proportionately decrease the salinity at Imperial Dam.

A quantitative analysis of the effects of the addition of salts as a result of oil shale operation is more difficult to determine, due, for example, to the uncertainty of the type and timing of the shale-processing technologies likely to be used, of the reliability of catchment basins against failure, or of the amount of percolation through ground-water/surface-water systems. A catchment basin failure or overflow would probably discharge to the surface waters a large volume of trace elements in a short time interval. Leaching to percolating ground waters, on the other hand, could result in slow but sustained movement of trace elements to surface-water systems. These factors and the possible mitigating effects of proper waste management and engineering design are discussed below in greater detail.

Retorting and Disposal

Three major types of solid and liquid waste may be disposed to the ground from above-ground retorting--off-gas scrubbing wastes, retorted shale, and retort process water. Because of the quantity produced, disposal of retorted shale will result in major redistribution of accessory elements.

Off-Gas Scrubber Wastes

Off-gases, including hydrogen sulfide, will undoubtedly be produced by retorting, and wastes from scrubber treatments of the off-gases may be disposed to the ground (Pfeffer and Kerr 1974). Information on the composition and consequences of disposal of these wastes is not available.

Retorted Shale

The quantity of retorted shale produced by a 1-million-barrel-per-day mature industry has been estimated to be 1.2 to 2.0 million tons per day (Hand 1969). Several kinds of disposal problems have been anticipated, including (1) selection of disposal location, (2) stabilization of the retorted shale against wind and water erosion, and (3) mitigation of the effects of retorted shale leachates.

An ideal method of disposal of retorted shale would be to return it to the mine, but the volume of the retorted shale is 10 to 25 percent greater than that of the dense, fine-grained unmined shale (Cook 1974b and Pfeffer and Kerr 1974). The porosity of unmined oil shale is low (<5 to 10 percent) compared to that of compacted retorted shale, which ranges up to 40 percent by volume depending on the amount of compaction (Cook 1974b). Thus, even if the original mines are completely filled with retorted shale, a considerable volume must be disposed of by other means. However, recovery of nahcolite and dawsonite as byproducts, in some locations, may permit the entire remaining volume of retorted shale to be returned to the mine (Weichman 1974b).

Retorted shale contains nominal quantities of oxides, which range from soluble (sodium) to slightly soluble (calcium and magnesium). The conversion of largely insoluble carbonates and other minerals to the more soluble oxides depends on the retorting temperature. Carbonates begin to decompose at 600°F, and at 1,500°F conversion is largely complete; heating rate and time are also important factors. Thus, the leachability of these elements will depend on the source of the shale and the retorting process. Disposal of retorted shales close to the water table or within the saturated zone would, however, present a potential source of ground-water pollution. It appears that, except for As, F, Hg, and perhaps Sb, most trace elements are conserved in the retorted shale, with lesser quantities in the shale oil. Comprehensive information on the leachability of trace metals in the retorted shale and its potential impact is not available.

In addition to mine filling, there are plans to emplace retorted shale in canyons near retorting operations (Hand 1969; Pfeffer and Kerr 1974; Cook 1974a, b; Fletcher and Baldwin 1973; Heley 1974; Hutchins et al. 1971; and Ward and Reinecke 1972). For this procedure, surface-disposal embankments must be carefully engineered, and control reservoirs, retaining dams, and water interception systems will be needed to collect runoff from possible summer flash floods and from snowmelt (Cook 1974a). Research by Development Engineering Incorporated at the Paraho retort site, Anvil Points, Colorado, indicates that a cross-valley dam of compacted retorted shale with a lining of compacted impervious shale would contain the disposed shale and leachates if upstream flows were diverted (Woodward-Clyde Consultants 1976). Studies of the four-year-old embankment at the Colony retorted shale disposal site at Parachute Creek indicate little moisture movement to depths below several feet (Merino and Crookston 1977). However, design and evaluation should consider possible catastrophic events and long-term climatic variations.

Unless stabilized, retorted shale is subject to water and wind erosion (Fletcher and Baldwin 1973). Compaction of shale and establishment of vegetative cover will be required to minimize the erosion of surface-disposed retorted shale (Heley 1974, Cook 1974a, and Fletcher and Baldwin 1973). To establish sufficient vegetation on retorted shale, soluble salts must be leached in conjunction with fertilization (nitrogen and probably phosphorus treatments) and irrigation (Schmehl and McCaslin 1973, and Cook 1974a). It has been estimated that water equivalent to a column 4 feet in height will be required to leach retorted shale adequately for plant growth (Cook 1974b), although preliminary evidence from studies in progress indicates that less water may be required. It has also been suggested that a layer of soil be used as a surface cover over the retorted shale (Schmehl and McCaslin 1973). Successful implementation of this treatment requires that the net movement of water be downward to avoid transport of salts from the retorted shale to the overlying soil, and to assure this, initial leaching of the retorted shale may be required (Bloch and Kilburn 1973). Leaching for these purposes increases the possibilities of redistribution of elements and of contamination of surface and ground waters.

As in the case of inorganic components, the concentrations of organic residues depend upon the character of the shale, retorting temperatures, oxygen concentration, and reaction kinetics. Thus, potential problems related to organic residues, such as complexing of trace elements and solubilization of the organic residues, will depend on the process and the management of the wastes as well as environmental variables such as changes in temperature and moisture with time. The effects of these variables on mobility of organic residues have not been studied.

Retort Wastes

Water will be produced during the retorting process. Although extensive organic characterization has been performed on shale oil, relatively little information is available on the properties of organic material in the retort waste water. Since the waste water contains soluble constituents from the oil, however, some insight into its organic composition may be obtained from studies of shale oil composition. Shale oil differs from petroleum crude oils in that it contains much higher concentrations of polar and heterocyclic components, particularly nitrogen compounds, which constitute 1 to 2 percent by weight (Jensen et al. 1971).

The environmental significance of the presence of polar and heterocyclic components in shale oil is two-fold. These compound types are potentially toxic, and their polar character may increase their solubility and entrance into water systems. The nature and extent of these phenomena as they relate to process variables and as they influence the mobility of inorganic and organic components of the retorted shale require study. However, it should be noted that if retort waste is applied to retorted shale for compaction, dust control, and reclamation, then sorption and degradation will occur with time. Furthermore, retort waste may be amenable to treatment by charcoal sorption, with eventual destruction of sorbed organic compounds by heating (Hubbard 1971).

INFORMATION AND RESEARCH NEEDS

The production of shale oil involves a unique technology with respect to processing, nature of product, and geography. Information necessary for a thorough evaluation of the effect of the several potentially commercial technologies on redistribution of accessory elements and associated environmental effects is not complete and/or fully available in the open literature.

In order to ensure an orderly development of the oil shale resource should it become necessary, it is highly desirable to continue study of the redistribution of accessory elements, and of associated environmental and health problems through a balanced, interdisciplinary research effort. Major components of this effort should include: (1) source characterization and monitoring, (2) atmospheric transport, (3) hydrologic transport, and (4) environmental effects. Efforts are under way in industry, federal agencies and their contractors, and the universities to meet these needs. At present, these research programs are not generally duplicative, due in part to early planning by several agencies, relatively low research and development expenditures, and the early stage of many of the programs. However, there is a need to collect, catalog, and evaluate pertinent data from past efforts in shale, coal, and mineral processing for use as a basis for early coordination of future research.

Process-Stream Characterization and Environmental Monitoring

The chemical and physical nature of materials that may reach the environment as a result of in situ and above-ground extraction, transportation, conversion, waste treatment, and final use of oil from shale must be determined in detail to provide the essential information for evaluation of air transport, water transport, ecological effects, and health effects, and for an integrated assessment of all of these factors. These measurements should encompass the major oil shale extraction processes, and should include determination of major organic compound classes (particularly amines, pyridines, pyrimidines, pyrroles, indoles, and polynuclear aromatics), of elemental composition (particularly N, S, Na, Cd, and Mg), and trace metals (particularly As, B, Cd, F, Hg, Ni, Pb, Sb, Se, Mo, V, and Zn). Toxic compounds that are identified should be determined quantitatively. Periodic measurements should be conducted on pilot projects, and should include, as appropriate, oil shale feedstock, crushing dust, retort water, retorted shale, off-gas, off-gas combustion products, waste water from scrubbers, cooling water from retort condensers, effluents from waste-treatment processes, shale oil, and various fractions from upgrading processes. The composition of these materials will be highly variable depending on the source of the material, process, and operating parameters. Thus, "representative" samples may not exist, and characterization efforts must be based on a detailed knowledge of the processes. Materials shown to be present in highest concentrations and having greatest potential for entrance into the environment should be the subject of environmental monitoring to provide a basis for assessment of ecological effects.

Development of accurate and reliable analytical techniques, particularly for trace organics, should continue, and emphasis should be placed on assuring comparability among investigators.

Atmospheric Transport

Although likely not a prerequisite for initiation of the oil shale industry, it would ultimately be desirable to develop a thorough understanding of transport, transformation, and diffusion processes in the atmosphere, and of the wet- and dry-deposition processes that deliver effluents to the terrestrial and aquatic environments. Evaluation of air quality should embrace a region sufficiently broad to include the probable sites of significant impact from oil shale development. These include multi-source emissions in the tri-state region of Colorado, Wyoming, and Utah. Projected changes in air quality should be interpreted on the basis of the natural background of the region.

Existing predictive models should be tailored to oil shale regions using information from source characterization and monitoring studies. The variation in height and direction of trajectory due to initial plume rise, terrain configurations, differential heating, surface roughness characteristics, and macroscale weather patterns should be incorporated in the models. Investigations are needed to evaluate resuspension processes and atmospheric particulate concentrations due to fugitive dust near development sites.

It is necessary to depict chemical and physical transformations of effluents, deposition of particulates and vapors, and the wet-removal processes. The influence of ground cover on deposition rates of particulates, gases and aerosols, and changes in deposition rates due to atmospheric transformations during transport should be given on-site study.

Meteorological data taken at the development sites should be used to delineate subregions of atmospheric homogeneity and their characteristics. A study region should be divided according to its varying degrees of complexity so that treatment of similar areas can be standardized and thus permit continued refinement and application of air quality modeling.

Field investigations should be undertaken to verify and modify the models for individual sources, as well as regional impacts due to combinations of primary and secondary sources. Field studies should include diffusion, entrainment in drainage winds, ventilation of air trapped in valleys, long-range transport of material in complex terrain, and wet and dry deposition and resuspension.

Hydrologic Transport

The water in the Green River Formation is a scarce and valuable commodity, and competition for water uses, such as water needed for processing and extraction requirements as opposed to the domestic needs of the expected increased population, may have significant social and political implications. Thus, with time, it will be desirable to develop a more complete quantification and understanding of the water resources of the region to fully determine the impact of proposed withdrawals and uses. Several key studies have been undertaken to assess the hydrology and movement of salts in the oil shale region. Current technologies appear capable of confining waste waters and residues, but there is a need to verify this at the semiworks scale for the different technologies.

To determine whether the control technology is adequate, it will be necessary to monitor the spatial distribution in water of the important mobile residues in a full-scale demonstration. This would provide a basis for detailed evaluation of environmental and health impacts.

Unified hydrologic and transport models are needed to assess the impact of water use and movement and the mobility of salts, trace metals, and trace organics in surface and ground waters. The studies should use the results of process-stream characterization, environmental monitoring, and meteorologic studies and should consider the possible deterioration of water quality and climatic changes over the long term (up to 100 years) and under different conditions, ranging from total containment to failure of catchment dams or retorted shale piles.

Environmental Effects

The geology, topography, vegetation, and wildlife, and the quality of surface and ground waters of specific parts of Piceance Creek Basin have been characterized in considerable detail. However, it is necessary to continue study of the nature and quantities of trace organics and trace metals in waste effluents, and their behavior, in laboratory and full-scale demonstrations, including the physical and chemical effects of using saline and retort waters to moisturize, compact, and thereby stabilize retorted shale disposal piles. Studies must also be undertaken to assess the possible changes which may occur with time and weathering, such as the formation of organic residuals and inorganic chemical complexes, perhaps through microbial activity, that might result in the formation of secondary organics and increase the solubility of certain elements. The findings of these studies should then be compared with background levels of these materials in leachates from soil and raw shales and in surface and ground waters of the Basin. It is important, for predictive purposes, to understand the mechanisms of transformation, solubilization, and redistribution of these accessory materials after disposal, as they are influenced by environmental factors over the long term. This information should then be used in determining uptake by flora and fauna, critical tolerance levels of key terrestrial and aquatic biota, and hazards or successional changes that may occur with elevation of residual levels.

APPENDIX TABLES AND FIGURES

TABLE A2.1 Elements Exceeding the Public Health Standards in Colony Development Property Ground Waters

Element	Concentration (mg/l)	
	Alluvial	Uinta and Green River Aquifers
Fluorine	NM(a)	1.5 - 6.0
Iron	0.77 - 57.0	0.8 - 44.0
Lead	0.06	0.06 - 0.2
Manganese	0.09 - 0.57	0.1 - 34.0
Selenium	NM	0.1
Sulfur (as SO_4^-)	280.0	260.0
Zinc	NM	6.6

(a) NM=Not measured

SOURCE: G.J. Saulnier, USGS, written communication (March 1977); U.S. Public Health Service (1962).

TABLE A2.2 Elements Exceeding the Public Health Standards in Federal Oil Shale Lease Tract C-b Ground Waters

Element	Concentration (mg/l)	
	Upper Aquifer	Leached Zone
Arsenic	0.06	0.83 - 22.0
Barium	1.3	5.0 - 8.0
Boron	1.3 - 18.0	200.0 - 405.0
Cadmium	NM(a)	0.1
Chlorine	514.0	270.0 - 9,820.0
Copper	3.0	NM
Fluorine	3.0 - 190.0	11.0 - 48.0
Iron	0.44 - 0.5	0.68 - 5.9
Lead	NM	0.4
Lithium	NM	39.0 - 79.0
Manganese	0.1 - 0.2	0.07 - 0.2
Mercury	0.0031 - 0.0024	NM
Selenium	0.02	0.02 - 21.0
Sulfur (as SO_4^-)	303.0 - 510.0	300.0

(a) NM=Not measured

SOURCE: G.J. Saulnier, USGS, written communication (March 1977); Tract C-b (1975); U.S. Public Health Service (1962).

TABLE A2.3 Elements Exceeding the Public Health Standards in Superior Oil Company Property Ground Waters

Elements	Combined Aquifers (mg/l)
Arsenic	0.46
Barium	3.2 - 3.9
Chlorine	270.0 - 830.0
Fluorine	7.6 - 95.0
Iron	2.2
Manganese	0.14 - 0.2
Sulfur (as $SO_4^=$)	314.0
Total dissolved solids	3,240.0 - 45,000

SOURCE: G.J. Saulnier, USGS, written communication (March 1977); B.E. Weichman, Superior Oil Co., written communication (April 1977); U.S. Public Health Service (1962).

TABLE A2.4 Elemental Concentration of Oil Shale from the Green River Formation on the Colony Development Property

Element	Concentration (ppm)	Element	Concentration (ppm)	Element	Concentration (ppm)
Li	850	Zr	9.3	Gd	0.40
Be	35	Nb	3.4	Tb	0.07
B	140	Mo	4.9	Dy	0.40
F	1,700	Ru	<0.1	Ho	0.07
Cl	72	Rh	<0.1	Er	0.27
Sc	2.4	Pd	<0.1	Yb	0.25
Ti	570	Ag	<0.01	Lu	<0.1
V	29	Cd	0.14	Hf	<0.1
Cr	49	In	standard	Ta	0.04
Mn	34	Sn	0.11	W	0.42
Co	39	Sb	0.39	Re	<0.1
Ni	11	Te	<0.1	Os	<0.1
Cu	15	I	<0.01	Ir	<0.1
Zn	13	Cs	1.2	Pt	<0.1
Ga	2.2	Ba	32	Au	<0.1
Ge	0.40	La	1.4	Hg	<0.1
As(a)	7.2(0.11)	Ce	1.6	Tl	0.14
Se	0.08	Pr	0.25	Pb	10
Br	0.01	Nd	1.2	Bi	0.36
Rb	29	Sm	0.44	Th	0.77
Sr	69	Eu	0.12	U	0.99
Y	1.2				

(a) Quantity in parentheses is water soluble.

SOURCE: An Environmental Impact Analysis for a Shale Oil Complex at Parachute Creek: Part 1, Plant Complex and Service Corridor. Colony Development Operation, Atlantic Richfield Company.

TABLE A2.5 Trace Element Concentrations in Shale Oils Produced by the TOSCO Process

Element	Raw Shale Oil (ppm)
Arsenic	50
Boron	10
Chromium	16
Copper	4
Fluorine	9
Lead	1
Mercury	3
Nickel	18
Vanadium	27
Zinc	130

SOURCE: R.G. Vawter, TOSCO Corporation, written communication (1977).

TABLE A2.6 Chemical Composition of Process Water from the TOSCO II Process

Component	Concentration (ppm)
Ca^{+2}	280
Mg^{+2}	100
Na^{+1}	670
NH_4^{+1}	15
Zn^{+2}	5
As^{+5}	(15 to 300 ppb)
Cr^{+6}	2
CO_3^{-2}	360
HCO_3^{-1}	100
SO_4^{-2}	850
$S_2O_3^{-2}$	90
PO_4^{-3}	5
Cl^{-1}	570
CN^{-1}	5
Phenols	315
Amines	410
Organic Acids	1,330
Neutral Oils	960
Chelates	5

In addition to above, elements present in trace quantities (less than 1 ppm) are Pb, Ce, Ag, Mo, Zr, Sr, Rb, Br, Se, Cu, Ni, Co, Fe, Mn, V, Ti, K, P, Al, F, B, Li.

SOURCE: U.S. DOI (1977).

TABLE A2.7 Trace Elements in Fractions from the Paraho Direct-Heated Retort Operated at Anvil Points

Element	Accessory Elements (ppm except as noted)				
	Retorted Shale	Oil	Retort Water	Retorted Shale Leachate	Stack Gas
Antimony	1	NM	1	NM	NM
Arsenic	30	20	.01	4	<.01(AsH_3)
Boron	65	NM	3	2	NM
Cadmium	NM	NM	0.5	<.01	NM
Fluorine	1000	NM	6	7	NM
Lithium	230	NM	1	NM	NM
Mercury	0.06	NM	<.01	.01	NM
Molybdenum	16	NM	0.1	4	NM
Selenium	0.5	NM	0.1	NM	NM
Sulfur	.8%	.6%	2.8%	400	1200
Nitrogen	.3%	2.0%	2.1%	NM	300

(a) NM=Not measured

SOURCE: J.B. Jones, Paraho Development Corp., written communication (1977).

TABLE A2.8 Concentration of Major Elements in Oil Shale and Accessory Minerals at the Superior Oil Company Site

Sample	Concentration (percent)								
	Al_2O_3	SiO_2	CaO	MgO	Fe	MnO	Na_2O	K_2O	TiO_2
Raw Outcrop Shale from Alumina Quarry	10.8	32.1	7.2	3.7	3.3	0.051	3.77	2.2	0.34
Raw Shale from Core Hole (1698'-1702') Alumina Quarry Equiv.	10.6	32.1	6.7	3.2	2.6	0.051	5.12	2.4	0.31
Raw Shale from Core Hole (1660'-1662') Nahcolite Quarry Equiv.	11.1	33.8	7.8	5.9	3.0	0.061	4.38	2.4	0.46
Raw Composite from Core Hole Proposed Mine Zone	6.5	23.1	10.9	4.5	2.3	0.046	9.4	1.4	0.19
80% Raw Nahcolite from Surface Outcrop	0.81	4.5	0.9	0.57	0.06	<0.003	32.4	0.4	0.39
Spent, Unleached Outcrop Shale from Alumina Quarry	13.41	42.8	8.5	4.1	4.6	0.056	4.79	2.5	0.39
Spent, Leached and Washed Shale from Alumina Quarry	11.1	46.4	9.1	4.3	5.0	0.072	4.18	2.6	0.43

SOURCE: B.E. Weichman, Superior Oil Co., written communication (1977).

TABLE A2.9 Concentrations of Trace Elements in Oil Shale and Extraction Products at the Superior Oil Company Site

Sample	Concentration in ppm, except Hg (in ppb)								
	Sb	As	B	Cd	F	Li	Hg	Mo	Se
Raw Outcrop Shale from Alumina Quarry	<2.5	25.0	21	<100	700	19.5	45.0	30	<5
Raw Shale from Core Hole (1698'-1702') Alumina Quarry Equiv.	<2.5	23.0	43	<100	800	24.0	38.4	31	<5
Raw Shale from Core Hole (1660'-1662') Nahcolite Quarry Equiv.	<2.5	17.0	69	<100	1300	30.6	34.0	36	<5
Raw Composite from Core Hole - Proposed Mine Hole	<2.5	15.0	16	<100	1200	21.7	32.6	32	<5
80% Ray Nahcolite from Surface Outcrop	<2.5	5.8	<10	<100	700	5.3	17.2	21	<5
Spent, Unleached Outcrop Shale from Alumina Quarry	<2.5	24.6	38	<100	800	20.6	4.8	28	<5
Spent, Leached and Washed Shale from Alumina Quarry	<2.5	13.4	32	<100	600	22.3	7.7	26	<5
Sour Retort Water (Alumina Quarry Shale) from Adiabatic Retort Run	<0.5	<1.0	NA(a)	<1.0	0.5	<0.1	225.0	1.0	<1.0
Oil - (Alumina Quarry Shale) from Adiabatic Retort Run	<2.5	<5.0	NA	<5.0	0.5	<0.5	250.0	9.3	<5.0

(a) NA=Not available

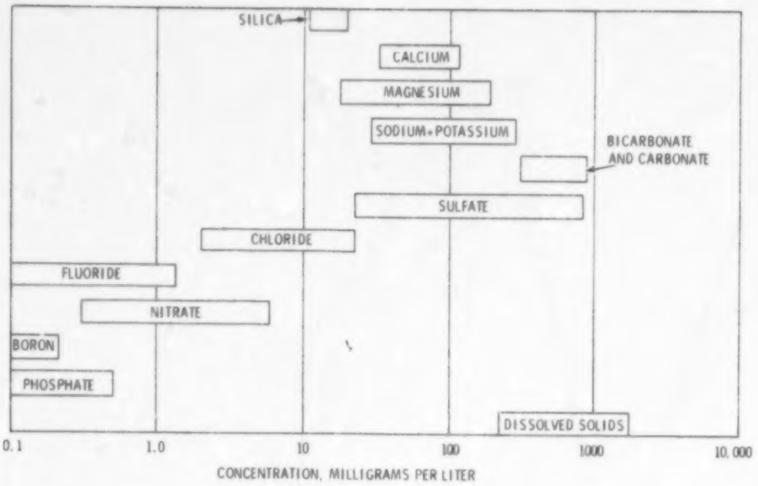
SOURCE: B.E. Weichman, Superior Oil Co., written communication(1977).

TABLE A2.10 Trace Element Concentrations in Oil Shale, Spent Shale, and Particulates near the Mine Site (ppm)

Sample	Sb	As	B	Cd	F	Li	Hg	Mo	Se
Raw Composite Shale from Proposed Mine Zone	<2.5	15.0	16	<100.0	1200	21.7	0.033	32.0	<5.0
Spent, Leached and Washed Shale from Alumina and Soda Ash Recovery	<2.5	13.4	32	<100.0	600	22.3	0.008	26.0	<5.0
High Volume Particulate Sample(a) Filter Analysis	4.4	22.8	<416	2.6	600	≈244.0	0.108	14.4	10.4

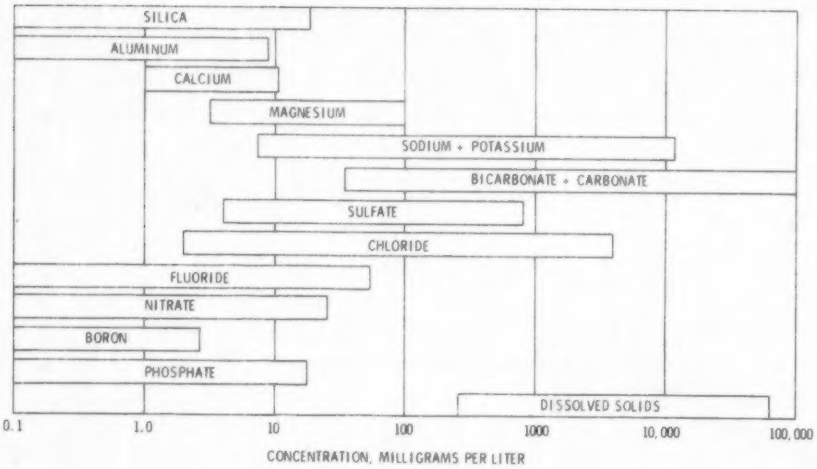
(a) From baseline data station located at mouth of Piceance Creek, Rio Blanco County, Colorado.

SOURCE: B.E. Weichman, Superior Oil Company, written communication (1977).



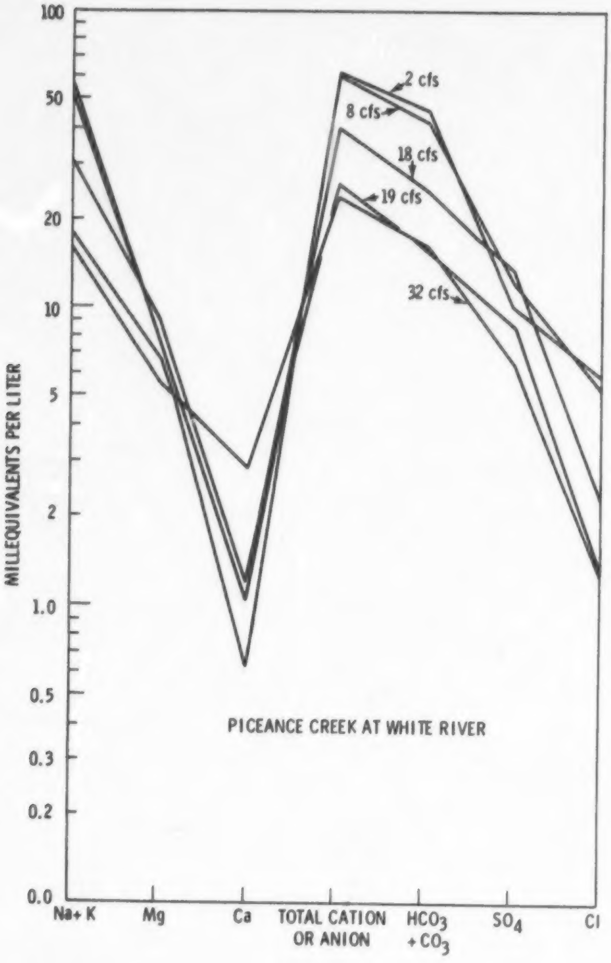
SOURCE: Coffin et al. (1971).

FIGURE A2.1 Range of water quality in the Evacuation Creek Member.



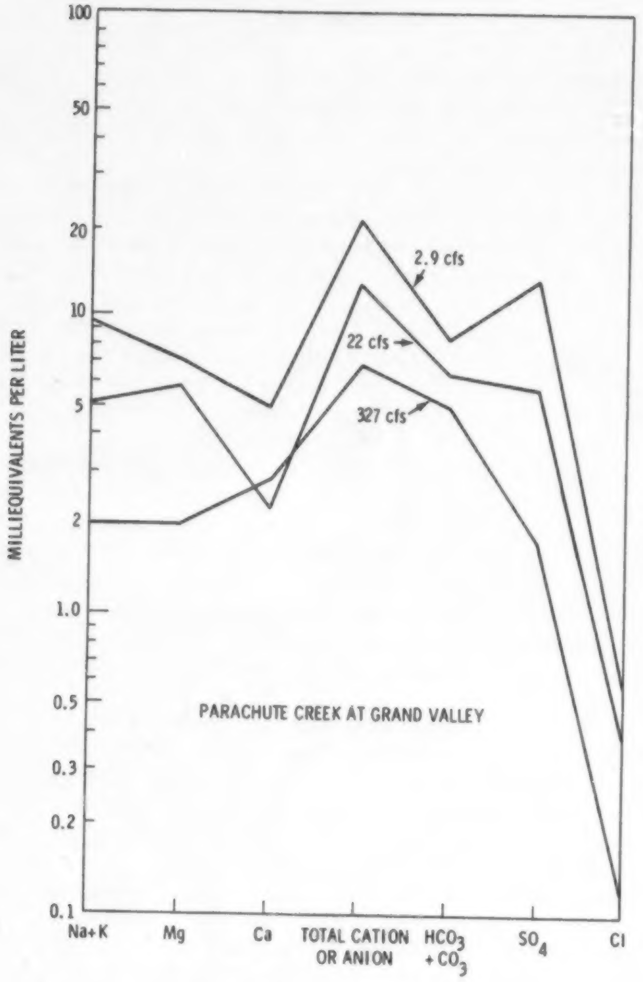
SOURCE: Coffin et al. (1971).

FIGURE A2.2 Range of water quality in the Evacuation Creek Member.



SOURCE: Coffin et al. (1971).

FIGURE A2.3 Range of concentrations in the surface waters of Piceance Creek as a function of flow rate.



SOURCE: Coffin et al. (1971).

FIGURE A2.4 Range of concentrations in the surface waters of Parachute Creek as a function of flow rate.

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